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**The Relation of Oxidant Levels to Precursor
Emissions and Meteorological Features. Volume II
Review of Available Research Results and
Monitoring Data (as of November 1975)**

SRI International, Menlo Park, Calif.

Prepared for

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**RELATION
OF OXIDANT LEVELS
TO PRECURSOR EMISSIONS
AND METEOROLOGICAL
FEATURES -**

**VOLUME II: REVIEW
OF AVAILABLE
RESEARCH RESULTS
AND MONITORING DATA**



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16. ABSTRACT This report was originally published as an Interim Report in November 1975. Literature available at that time was reviewed and a summary was prepared describing the processes affecting ozone concentrations in remote areas. The topics discussed include ozone of stratospheric origin, natural tropospheric sources and sinks, and long range transport in the troposphere. Selected research studies are abstracted and 38 sources of ozone or oxidant data taken at remote locations are discussed. A bibliography is included.		
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**Volume II: Review of Available Research Results
and Monitoring Data
(As of November 1975)**

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CONTENTS

I	BACKGROUND, OBJECTIVES, AND LIMITATIONS OF THIS REVIEW	1
II	REVIEW OF THE CURRENT STATE OF KNOWLEDGE ON THE RELATION OF OXIDANT LEVELS TO METEOROLOGICAL FEATURES	3
	A. Historical Overview.	3
	B. The Stratosphere as a Source of Tropospheric Ozone	7
	C. Natural Sources and Sinks of Ozone in the Troposphere	22
	D. Long-Range Transport and the Nonurban Oxidant Problem . .	23
	E. Summary of Significant Scientific Findings	31
III	DESCRIPTION OF SELECTED RESEARCH STUDIES	35
IV	SUMMARY OF AVAILABLE SOURCES OF OXIDANT/OZONE DATA	67
V	REFERENCES AND COMPREHENSIVE BIBLIOGRAPHY	107

I BACKGROUND, OBJECTIVES, AND LIMITATIONS OF THIS REVIEW

This review is a part of a research study being conducted for the U.S. Environmental Protection Agency (EPA). The overall study aims to answer the following questions:

- What causes the high oxidant values that are frequently observed in rural areas well removed from emission sources?
- What are the effects of synoptic and smaller-scale meteorological variables on ground-level oxidant concentrations?
- How much does ozone of stratospheric origin contribute to ground-level oxidant concentrations?
- Is it possible on the basis of relationships between oxidant concentrations and synoptic-scale meteorological conditions to identify geographic regions for uniform oxidant control strategies? If so, how?

As a logical first step in this effort, a relatively comprehensive survey of the relevant available literature and data has been carried out and is presented here. The objectives of this review are to:

- Develop a clear picture of the current scientific consensus on the oxidant problem in the eastern United States, with particular emphasis on the relation of nonurban oxidant to meteorological processes.
- Provide a compilation of appropriate available data as a basis for selection of the most available data from specific sites for further detailed analysis.

Accordingly, Sections II, III, and IV of this report provide an overview of the current state of knowledge on the oxidant problem, a descriptive listing of selected research studies, and a summary of available data sources, respectively.

Since the oxidant problem in the eastern United States is the topic of this investigation, studies and data dealing specifically with the West Coast oxidant problem have generally not been included in this report.

II REVIEW OF THE CURRENT STATE OF KNOWLEDGE ON THE RELATION OF OXIDANT LEVELS TO METEOROLOGICAL FEATURES

A. Historical Overview

In the early part of this century it was discovered that ozone* is synthesized in the stratosphere by chemical processes that involve photodissociation of molecular oxygen. It was found that O_3 has a unique vertical distribution with a maximum concentration of about 5-10 ppm (10^6 v/v) occurring at about 25 km (Junge, 1963). Thus the largest natural source of ozone was discovered and found to be extremely important in providing a protective (UV) shield against ultraviolet radiation for the earth.

In the early 1940s ozone was also found to be a tropospheric constituent, and the primary source was proposed to be the stratosphere. In the intervening years, it has been postulated that the downward transport of stratospheric ozone is controlled by air exchange mechanisms across the tropopause or through tropopause gaps, particularly in the vicinity of the jet stream and weather frontal zones (EPA, 1970).

Ozone took on a new role in the 1950s when it was discovered that ozone could be synthesized in the polluted air of cities by photochemical processes involving reactions between hydrocarbons and oxides of nitrogen (Leighton, 1961). Bell (1959) showed that ozone or ozone precursors could persist overnight and appear at high concentrations the next

* In this report, the terms "ozone" and "oxidant" are used interchangeably for convenience, since the models predict ozone and the standards apply to oxidants, and the difference between the two is not important in our discussion.

morning at distances as far as 100 miles away from their apparent sources in southern California. At this time it was still believed that the principal source of world-wide tropospheric ozone was the stratosphere, since ozone produced in polluted urban areas was considered to be only a localized problem, not contributing significantly to the global budget.

Based upon observed O_3 concentrations and diffusion theory, Frenkiel (1960) and Paetzold (1961) concluded that there must be a large tropospheric source of ozone. McKee (1961), from the vertical distribution of O_3 measured over Greenland, concluded that there must be local O_3 synthesis.

Went (1960) became the first to propose that natural ozone synthesis could take place in the troposphere in a manner similar to ozone synthesis in polluted air, with "terpenoid" compounds emitted by vegetation replacing the simpler olefins of the polluted air. Based on subsequent measurements, it was confirmed that both natural terpenes and NO_2 (as NO) are emitted in great enough quantities to influence O_3 concentrations in the troposphere (Rasmussen and Went, 1965; Lodge and Pate, 1963; Worth et al., 1967).

During the 1960s ozone began to draw serious attention as a pollutant in urban areas with a potential for both health and plant damage. The primary precursors were identified as hydrocarbons and oxides of nitrogen emitted by both mobile and stationary sources. The focus of photochemical pollution problems became Los Angeles, because of large numbers of automobiles, intense sunlight, and meteorological features leading to stagnation of air and trapping of pollutants. The diurnal variation of O_3 was recognized, with ground-level ozone values starting near zero in the early morning, building to a maximum in the late afternoon, and then decreasing to low levels again by late evening. Limited

measurements in other urban areas demonstrated by the late 1960s that photochemical pollution, while most severe in Los Angeles, was to be found in almost all urban locations (NAS, 1974; Rubino, 1975; Jacobson and Salotollo, 1975; Hawke, 1974).

By 1970 the EPA promulgated National Ambient Air Quality Standards (NAAQS) for oxidants at 0.08 ppm, not to be exceeded more than once a year (EPA, 1970). To achieve this standard, abatement programs were undertaken and further steps proposed to limit hydrocarbon and NO_x emissions as a means of controlling oxidants. EPA has published procedures for determining the necessary precursor reductions (Federal Register, 1971) to be applied in local areas in which a measurable oxidant problem exists. At this time, it was still believed that ozone was a local urban problem only and that diffusive and destructive processes limited the oxidant concentrations in rural areas to insignificant levels. Therefore, control strategies (Federal Register, 1971) were based primarily on emission controls at locations in which a photochemical oxidant problem was observed.

However, in a study conducted by EPA in 1970 in a rural area of western Maryland and eastern West Virginia, oxidant values exceeding the NAAQS were frequently measured. This finding was responsible for the subsequent initiation of a number of intensive field studies covering a broad area east of the Mississippi River. It was discovered that high oxidant concentration was not limited to any given rural location but was a widespread phenomenon.

While there is no doubt that high oxidant values can be measured in rural and remote locations, the sources have become a matter of considerable controversy. It is agreed qualitatively that stratosphere and natural ozone precursors contribute to the tropospheric background. The possibility of other tropospheric sources (Chemides and Walker, 1973)

cannot be ruled out. It is also becoming more evident that processes that destroy ozone or ozone precursors are not as effective as initially believed, and large-scale transport from urban to rural areas may be a key aspect of the oxidant problem. On the basis of several recent studies, it has become clear that sources of nonurban ozone must be identified before effective control strategies can be developed.

The implications of these findings may be significant for control strategies at the national level, as discussed by Altshuller (1975). For example, regional-scale control strategies may be required to achieve the NAAQS if long-range transport of ozone is found to be important. If the "natural" ozone concentration is in excess of the current standards, the standards are too stringent.

In subsequent sections we will review the available scientific literature that deals with the following major questions:

- How much of the tropospheric oxidant can be attributed to stratospheric exchange processes, and how do these processes occur?
- What are the natural tropospheric sources and sinks of oxidant, and what is their significance to the oxidant budget?
- What is the geographical extent of the transport of oxidant or oxidant precursors, and what is its effect on air quality control strategies?

Considerable overlap between these questions occurs in the available research papers. This is to be expected since the ultimate explanation of oxidant behavior is likely to involve a number of different mechanisms.

B. The Stratosphere as a Source of Tropospheric Ozone

1. Mass Exchange Mechanisms

The exchange of air masses between stratosphere and troposphere is accomplished by various mechanisms of different efficiency. These mechanisms are summarized below.

a. Seasonal Adjustments in the Height of the Mean Tropopause Level

In spite of some ambiguities in the definition, and therefore in the exact location, of the tropopause level, it is evident from statistical studies that this level in each hemisphere undergoes seasonal fluctuations, becoming lower during fall and higher during spring. Staley (1962) pointed out that his seasonal variation contributes towards a net flux of air between stratosphere and troposphere, upward or downward, depending on the season. The lowering and rising of the tropopause should not be envisioned as a continuous process, however. It comes about by an imbalance between the vertical mass fluxes produced by the mean Hadley circulation in low latitudes and by the eddy transport processes mainly in the jet-stream region of middle latitudes. There also is a compensatory horizontal mass flux within the stratosphere, directed from the summer to the winter hemisphere.

Table 1 (Reiter, 1975a) provides an estimate of changes in the median tropopause pressure over North America between January 1963 and July 1963. Since the total mass of stratospheric air above the winter tropopause is approximately 4260×10^{17} g, the seasonal variation of tropopause heights over North America--when applied to the whole northern hemisphere--amounts to approximately 10 percent of the mass equivalent to one hemispheric stratosphere.

Table 1
SEASONAL VARIATION OF MEDIAN TROPOPAUSE PRESSURES
(IN MILLIBARS) OVER NORTH AMERICA
(Reiter, 1975a)

Latitude (deg)	Tropopause Pressures (mb)		Δp	Mass Change (10^{17} g)
	Winter	Summer		
0			+(25)	+28.4
5			+(25)	+56.7
10			+(25)	+55.6
15			+(25)	+55.0
20	95	120	+25	+53.3
25	100	120	+20	+41.3
30	160	120	-40	-78.9
35	200	120	-80	-148.8
40	220	120	-100	-174.6
45	250	140	-110	-177.1
50	250	200	-50	-72.6
55	240	210	-30	-38.8
60	225	225	0	0
65	230	230	0	0
70	240	240	0	0
				-400.5

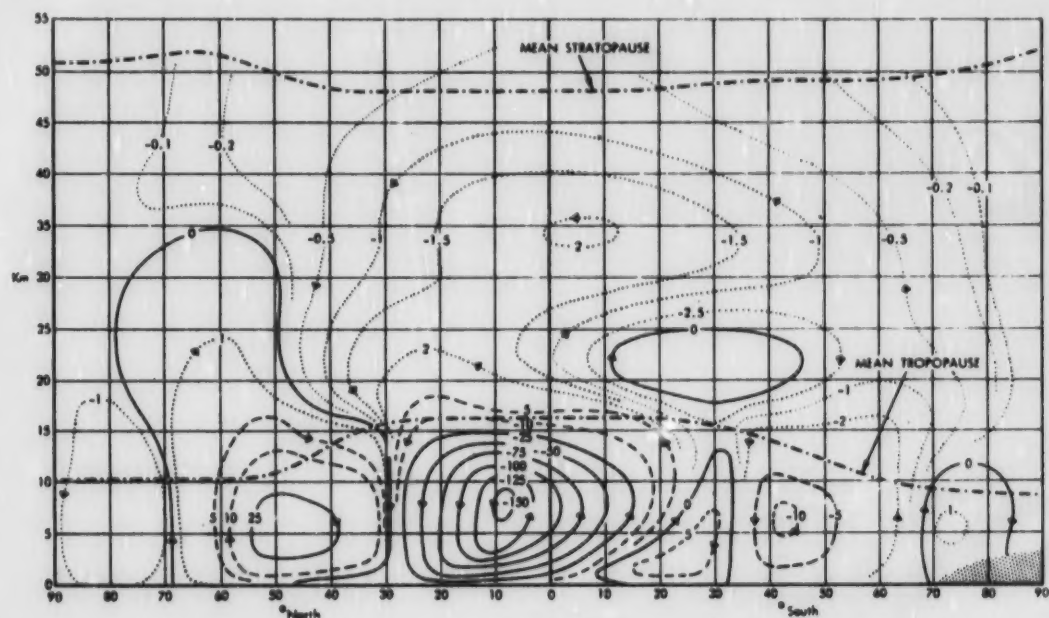
b. Transport by the Mean Meridional
Circulation Across the Tropopause

Figure 1 (from Louis, in Reiter et al., 1975) shows the distribution for the four seasons of the integrated mean meridional mass flux, ψ , i.e., the mass-weighted stream function defined by

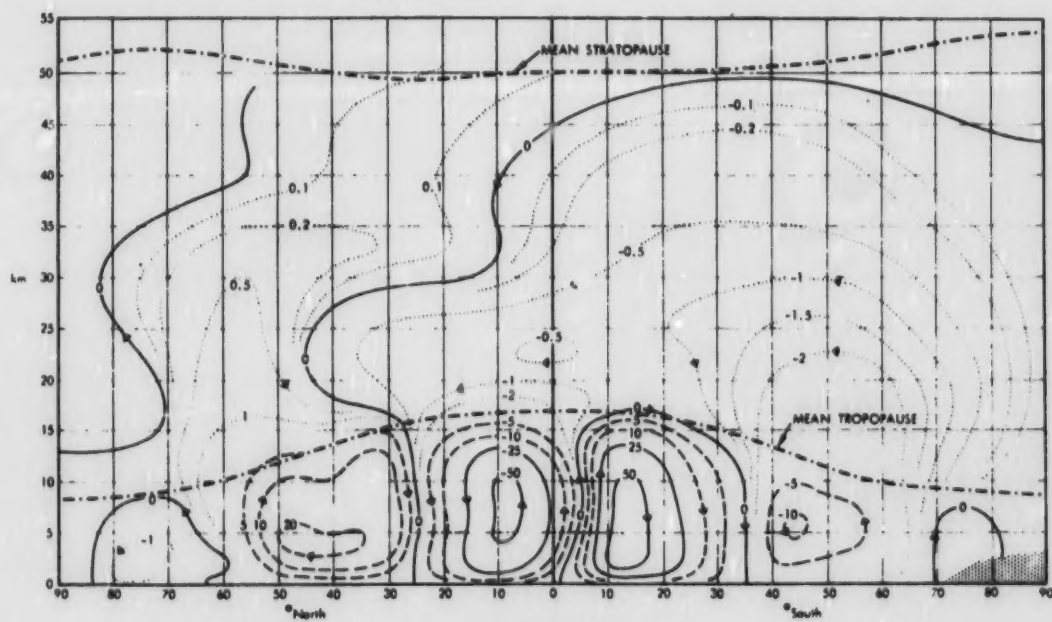
$$\bar{v} = \frac{1}{2\pi R \rho} \frac{\partial \psi}{\partial z} \quad (1)$$

$$\bar{w} = \frac{1}{2\pi R^2 \rho \cos \phi} \frac{\partial \psi}{\partial \phi} \quad (2)$$

where $\bar{v}$ is the northward component
 $\bar{w}$ is the vertical component
 R is radius of the earth
 ρ is air density
 ϕ is latitude



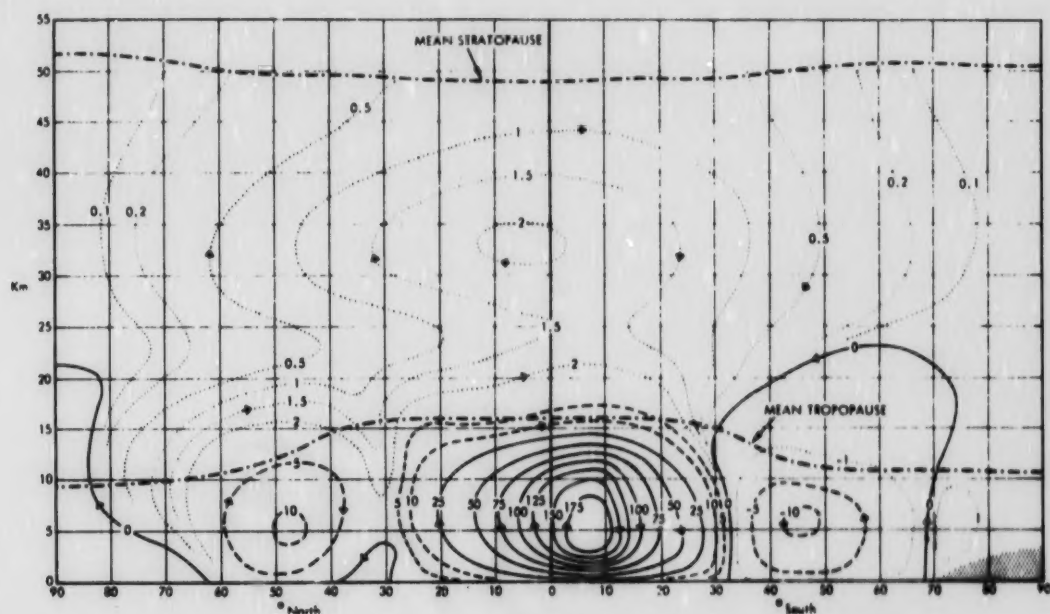
(a) DECEMBER-FEBRUARY



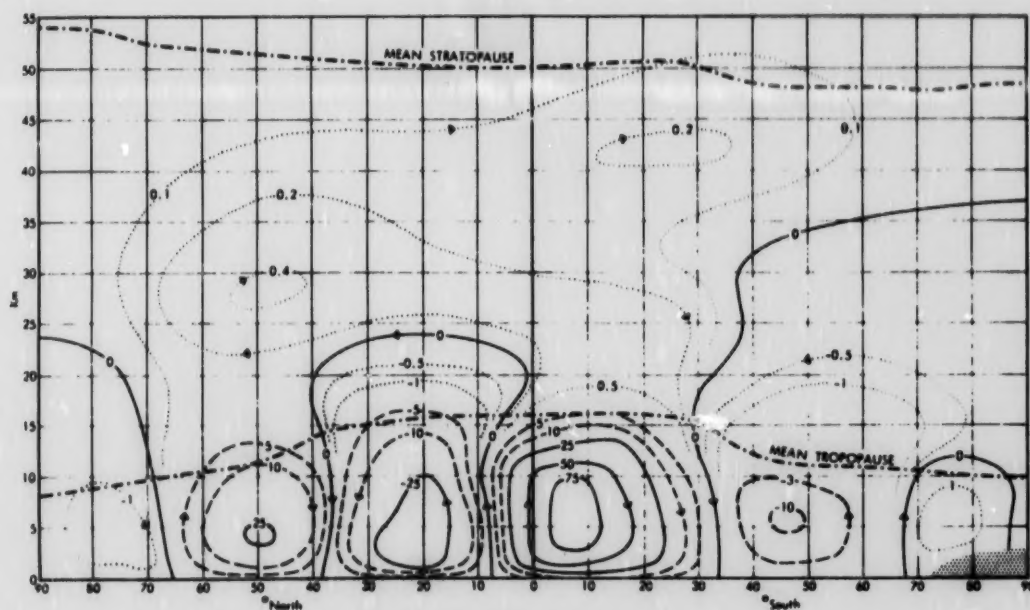
(b) MARCH-MAY

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FIGURE 1 MEAN MERIDIONAL CIRCULATION (MASS FLOW IN UNITS OF 10^{12} g s^{-1}) FOR THE FOUR SEASONS (From Louis)



(c) JUNE-AUGUST



(d) SEPTEMBER-NOVEMBER

SA-4432-3

FIGURE 1 MEAN MERIDIONAL CIRCULATION (MASS FLOW IN UNITS OF 10^{12} g s^{-1}) FOR THE FOUR SEASONS (From Louis) (Concluded)

The upward fluxes from the troposphere into the stratosphere and consequently, for reasons of continuity, the downward fluxes into the troposphere accomplished by the Hadley circulation, can be obtained from Figure 1 as follows:

<u>Season</u>	<u>Mass Flow</u>	<u>Total Flux in 3 Months</u>	<u>Contribution to Northern Hemisphere</u>
Dec. - Feb.	10×10^{12} g/s	788×10^{17} g	622×10^{17} g
March - May	4×10^{12} g/s	311×10^{17} g	272×10^{17} g
June - August	7.5×10^{12} g/s	583×10^{17} g	389×10^{17} g
Sept. - Nov.	7×10^{12} g/s	544×10^{17} g	560×10^{17} g
Annual total flux to northern hemisphere:			1843×10^{17} g

This flux corresponds to 43 percent of the mass equivalent to one hemispheric stratosphere.

c. Transport by the Mean Meridional Circulation into the Other Hemisphere

From Figure 1 we can also estimate the interhemispheric exchange of mass within the stratosphere as a function of season. We arrive at the following numbers:

<u>Season</u>	<u>Mass Flow</u>	<u>Total flux in 3 months into Northern Hemisphere (+)</u>
Dec. - Feb.	6.5×10^{12} g/s	505×10^{17} g
March - May	2.0×10^{12} g/s	156×10^{17} g
June - August	-6.5×10^{12} g/s	-505×10^{17} g
Sept. - Nov.	-2.0×10^{12} g/s	-156×10^{17} g

The mass flux between the stratospheres of the two hemispheres, thus, replaces 661×10^{17} g of mass from one hemisphere within one year. This is equivalent to 16 percent of the mass of one hemispheric stratosphere.

d. Transport by Large-Scale Eddy Exchange, Mainly
in the Mid-Latitude Jet-Stream Region

Intrusion of stratospheric air into the troposphere by large-scale eddy exchange occurs mainly within the jet-stream front during the tropopause-folding process, i.e., during periods of active cyclogenesis. A number of case studies illustrating this mass-transfer process are available in the literature (e.g., Danielsen, 1960, 1961, 1964, 1968; Danielsen et al., 1970; Mahlman, 1964a, b, 1965a, b, 1966; Reiter, 1963b, c, 1964, 1968; Reiter et al., 1969; Reiter and Mahlman, 1964, 1965a, b, c, d; Staley, 1960, 1962). The return flow of tropospheric air into the stratosphere occurs at levels above the jet-stream fronts and at potential temperatures characteristic of the core of the jet-stream itself (Reiter et al., 1969).

Only very few studies are available that give quantitative estimates of this eddy flux across the tropopause level (Danielsen, 1960; Reiter and Mahlman, 1965; Reiter et al., 1969). Our best guesses indicate that 22 to 23 cyclogenetic events occur per year in the polar-front jet-stream region of the North American longitude sector, with an average mass transport contribution of about 6×10^{17} g each, providing an annual mass flux out of the stratosphere of approximately 135×10^{17} g in the sector 70° to 180° W, and of approximately 405×10^{17} g around the hemisphere. This number includes only the latitude belt 40° to 60° N. If one were to allow for the effects of the subtropical and arctic-front jet streams of winter, and of the tropical easterly jet stream of summer, one might estimate the total eddy mass flux from the stratosphere to the troposphere to be 800×10^{17} g. For reasons of mass continuity, an equal amount of tropospheric air will have to enter the stratosphere in eddy exchange processes. This flux corresponds to roughly 20 percent of the mass equivalent to one hemispheric stratosphere.

e. Meso- and Small-Scale Eddy Transport Processes

Thunderstorms penetrating the tropopause level, as well as small-scale turbulence continuously present in the atmosphere, will contribute in a minor way towards the mass exchange between troposphere and stratosphere. Since these processes are either very slow-acting (due to the relatively small vertical eddy exchange coefficients normally effective at tropopause level), or are present with significant magnitude only sporadically (e.g., clear-air turbulence at tropopause level, or thunderstorms penetrating the tropopause), the total contribution towards the mass flux from the stratosphere to the troposphere from meso- and small-scale eddy processes most likely lies near 1 percent of the mass equivalent to one hemispheric stratosphere.

2. Implications on Ozone Transport from the Stratosphere

From the foregoing discussion the annual mass budget of the stratosphere of the northern hemisphere appears as follows:

Seasonal adjustments of tropopause level	10%
Mean meridional circulation	43%
Stratospheric exchange between hemispheres	16%
Large-scale eddies	20%
Small-scale eddies	<u>negligible</u>
Total:	89%

These transport processes would act on an atmospheric tracer that has been introduced into the northern hemisphere stratosphere and disperses from there into the northern hemisphere troposphere and into the southern hemisphere stratosphere. A typical tracer of this sort is ^{90}Sr , injected in large quantities into the northern hemisphere lower and middle stratosphere during the US and USSR atmospheric tests before the Test Ban Treaty went into effect in 1963. Figure 2 illustrates a typical ^{90}Sr distribution in the stratosphere.

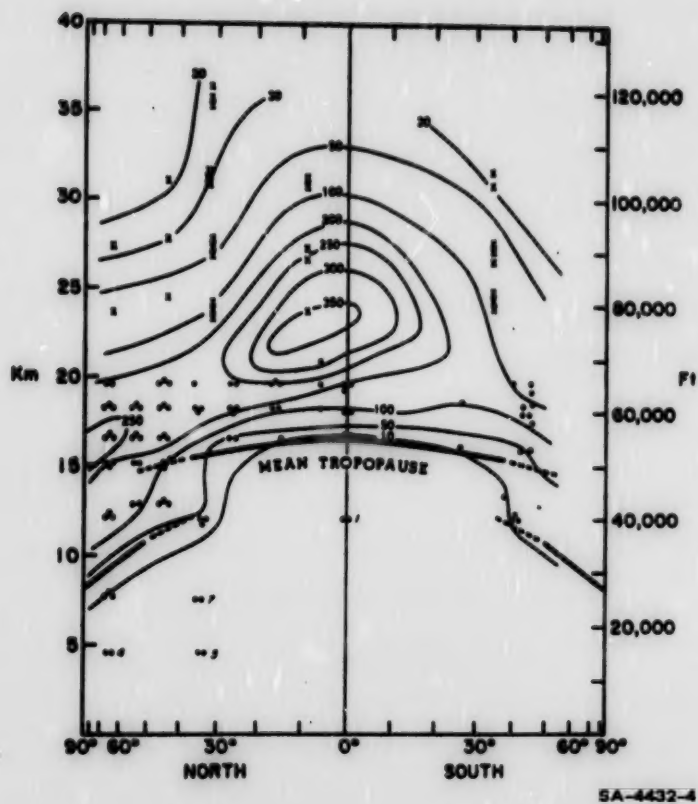


FIGURE 2 ^{90}Sr CONCENTRATIONS DURING MARCH-MAY 1965 IN UNITS OF DISINTEGRATIONS PER MINUTE PER 1000 STANDARD FT^3
Decay corrected to time of sampling. Dots show location of mean aircraft data; crosses indicate mean balloon samples. (From *List and Telegadas*, 1969)

Figure 3 shows the northern and southern hemispheric burdens of ^{90}Sr , as well as the total stratospheric burden, as functions of time. The e-folding residence time of ^{90}Sr in the northern hemisphere appears to be 14 months (before the effects of the French and Chinese tests). If we assume that concentrations of radioactive debris, N , diminish according to

$$\frac{\Delta N}{\Delta t} = -\frac{1}{T} N \quad (3)$$

where T is the e-folding residence time, N is taken to be 100 percent, ΔN is 89 percent and Δt is one year, we arrive at $T = 1.12$ years or 13.4 months.

According to Figure 3, the e-folding residence time in the southern hemisphere stratosphere appears to be of the order of 21 months. Assuming that the mean meridional and eddy exchange processes between stratosphere and troposphere are as effective in the southern as in the northern hemisphere, we have to blame the discrepancy in e-folding residence times between the two hemispheres on the following fact: inter-hemispheric exchange processes within the stratosphere tend to reduce the radioactive burden of the northern hemisphere where the original source was located. At the same time this transport process increases the southern hemisphere burden. Therefore, in approximation we can write

$$\frac{\Delta N}{\Delta t} = -\frac{1}{T} N + S \quad (4)$$

where S (= 16 percent, the stratospheric mass exchange between hemispheres) is the "source" of stratospheric debris for the southern hemisphere in the form of transport from the northern hemisphere. This 16 percent contribution towards the mass budget of the stratosphere now appears as a "source" of debris and has to be removed from the "sink" effects of the mass budget. Therefore, for the southern hemisphere, we

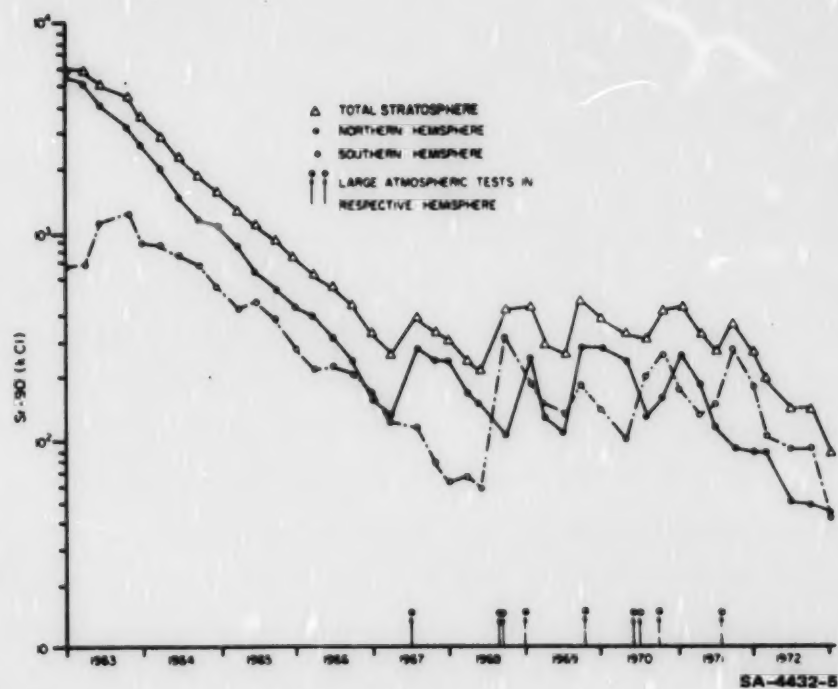


FIGURE 3 STRATOSPHERIC INVENTORY OF ^{90}Sr (From Krey *et al.*, 1974)

have to assume a value of 73 percent for ΔN (89% - 16%). For $N = 100$ percent and $\Delta t = 1$ year, we thus arrive at $T = 1.75$ years or 21 months, which is exactly what Figure 3 indicates.

E-folding residence times for other radioactive tracers introduced into the lower and middle stratosphere under similar conditions yield similar residence times (for references see Reiter, 1975b).

The above discussion leads us to the following preliminary conclusions:

- The estimate of an annual exchange of 16 percent of the mass equivalent to one hemispheric stratosphere appears to be accurate when applied to tracers in the lower and middle stratosphere.
- The total effects of other transport processes listed above have been estimated with similar reliability.

The mixing ratios of ozone, as reported by Newell (1964) (see Figure 4), show a distribution with respect to latitude and height that is similar to that for ^{90}Sr . The axis of maximum ozone mixing ratios dips downward from the equator to high latitudes, similar to the axis of maximum ^{90}Sr concentrations (see Figure 5 for similar evidence from additional other tracers).

Since the photochemical life-time of O_3 is relatively long at levels below 25 km (for references see Reiter, 1971 and Reiter et al., 1975) we can regard it almost as an inert tracer when comparing it, for instance, with ^{90}Sr . However, the following exception applies: in contrast to ^{90}Sr , O_3 is produced in both hemispheres. Interhemispheric transport processes within the stratosphere, therefore, will have no profound effect on the mean residence time of O_3 . To calculate the mass budget of one hemisphere, as it applies to ozone, we thus use Equation (3), with a value $\Delta N = 73$ that includes all effects except the one from interhemispheric exchange. The e-folding residence time of O_3 in the

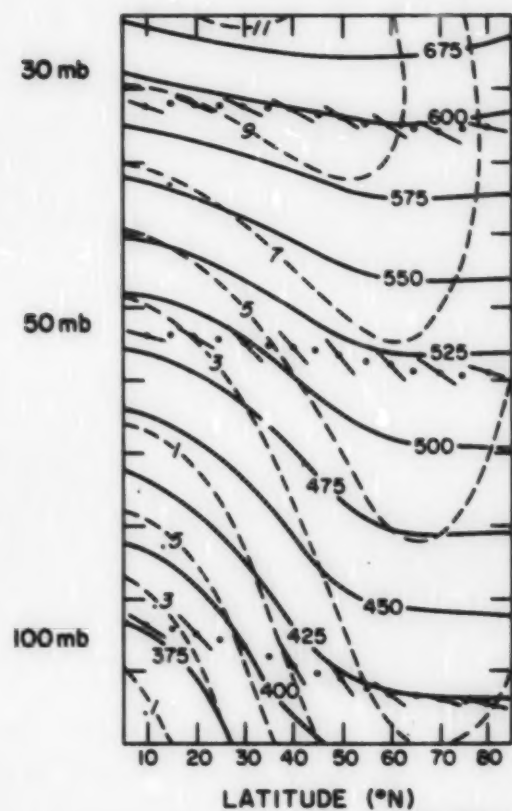


FIGURE 4 SLOPES OF SURFACES OF PREFERRED MIXING (SHORT LINE SEGMENTS) FOR WINTER SEASON AS DERIVED FROM HEAT FLUX DATA

Solid lines represent mean potential temperature ($^{\circ}\text{A}$) and dashed lines mean ozone mixing ratio ($\mu\text{gm/gm}$) after Newell (1964). (From Reed and German, 1965)

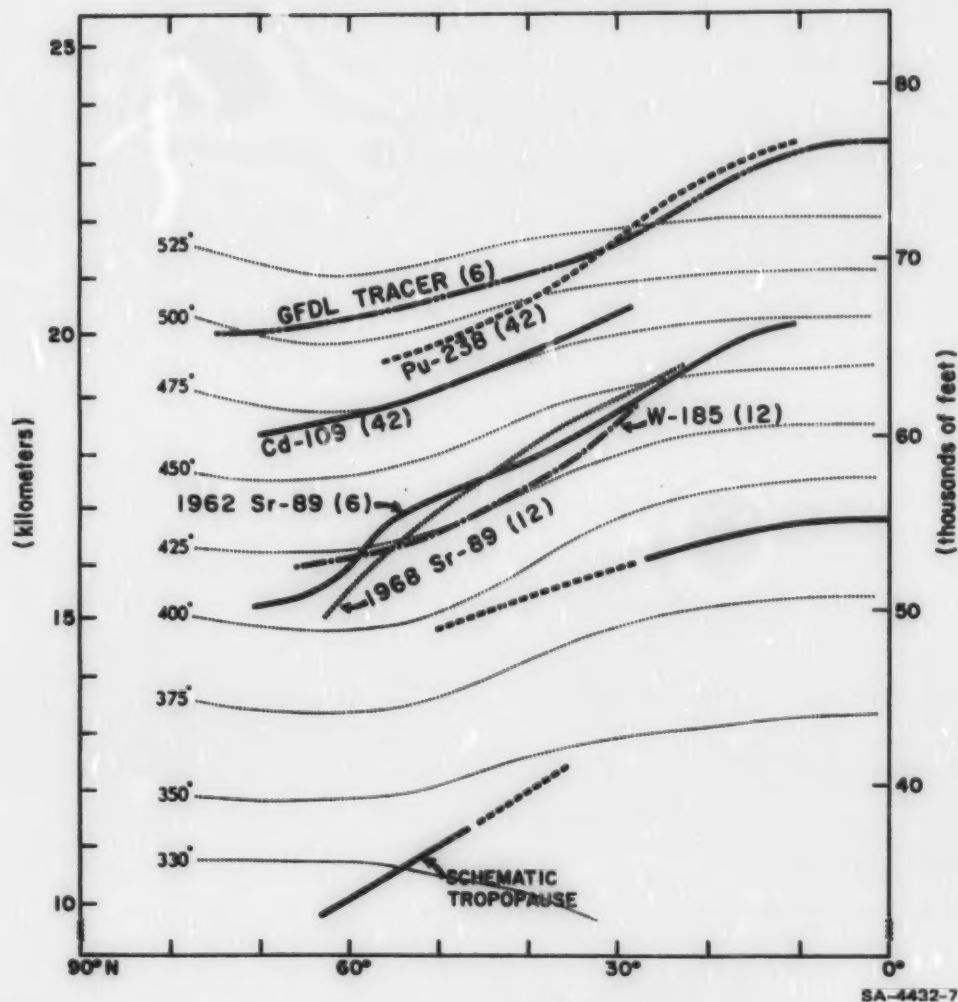


FIGURE 5 OBSERVED LEVELS OF MAXIMUM CONCENTRATION AND MEAN ANNUAL ISENTROPES

Numbers in parentheses are months from injection into the stratosphere to observation (From Machta et al., 1970)

lower and middle stratosphere, therefore, should be of the order of 1.4 years or approximately 16 months (similar to the e-folding residence time of ^{90}Sr in the total stratosphere as shown in Figure 3).

It is not surprising that estimates of the O_3 residence time in the stratosphere made from the phase lag between the maximum in total O_3 and that in surface O_3 concentrations are much larger than this estimate of 16 months. Junge (1962, 1963) and Fabian and Junge (1970) arrive at a stratospheric residence time of three to five years, a tropospheric residence time of 3.3 months, and a tropospheric vertical flux of approximately $0.5 \times 10^{-7} \text{ g/m}^2/\text{sec}$ (equivalent to 0.804×10^9 tons of O_3 per year over the entire globe). A vertical flux of 1.3×10^9 tons of O_3 per year over the globe was estimated by Regener and Aldaz (1969). Since O_3 is continuously generated photochemically in the stratosphere, Equation (3) is inapplicable, even for a crude estimate of residence time. Influx of O_3 from higher levels and from lower latitudes also provides a source for the atmospheric "box" that comprises the northern hemisphere stratosphere between the tropopause and approximately 30 km.

From satellite data, Lovill (1972) estimates the average global value of total ozone to be 303.3 Dobson units (or milli-atmospheric-centimeters, i.e., the height of the layer in units of 10^{-3} cm if all ozone were compressed to normal temperature and pressure). To convert these units into mass of ozone we apply the gas law

$$p = \frac{R^*}{m} \rho T, \quad (5)$$

where $p = 1013.25 \times 10^3 \text{ dynes/cm}^2$, the universal gas constant $R^* = 8.31436 \times 10^7 \text{ erg mole}^{-1} \text{ deg K}^{-1}$, the molecular weight of ozone, $m = 47.998$, $T = 273.16 \text{ deg K}$. We arrive at a density for ozone of $\rho = 2.14138 \times 10^{-3} \text{ g/cm}^3$, at normal temperature and pressure. The weight of the average ozone column, therefore, is $6.4948 \times 10^{-4} \text{ g/cm}^2$.

On a hemispheric basis (area = $2.55 \times 10^8 \text{ km}^2$) this amounts to $1.6565 \times 10^{15} \text{ g}$, or $1.6565 \times 10^9 \text{ tons}$.

The annual downward flux in one hemisphere ($0.402 \times 10^9 \text{ tons}$) thus corresponds to approximately one-quarter of the total atmospheric burden. Dividing the latter by the former to arrive at a crude measure of residence time (Ehhalt, 1973) one obtains a value of about four years, which falls within the range given by Junge.

Since the average tropospheric ozone mixing ratio of the troposphere is $\ll 0.1 \text{ } \mu\text{g/g}$, the tropospheric ozone burden in one hemisphere is much less than $1.3 \times 10^3 \text{ tons}$. Therefore, we can ascribe $1.65 \times 10^9 \text{ tons}$ of ozone to the hemispheric stratosphere.

According to estimates described earlier, in one year approximately 73 percent of the stratospheric air containing this amount of ozone should be transported into the troposphere by various mechanisms. This would correspond to an annual hemispheric ozone flux of $1.2 \times 10^9 \text{ tons}$, a value that is almost twice as high as the estimates by Regener and Aldaz and higher yet than those made by Junge. Eddy transport mechanisms in the jet-stream region should account for a flux of 20 percent of $1.65 \times 10^9 \text{ tons}$, i.e., for $0.33 \times 10^9 \text{ tons}$, which is not far from the value estimated by Junge from the phase lag between the maximum in total ozone and that in surface ozone. Since the latter--similar to the spring maximum of radioactive fallout--can be ascribed to the enhanced eddy activity in the jet-stream region during that season, Junge's estimates are comparable with effects that can be expected from these large-scale eddy exchange processes.

Even though the eddy exchange processes in the jet-stream region account for only a fraction of the total mass exchange between stratosphere and troposphere, they constitute the only mechanism which transports stratospheric air rapidly and relatively undilutedly towards the

ground. In the further investigation of the impact of stratospheric ozone concentrations on ground-level ozone concentrations, we will therefore concentrate our attention almost exclusively on this transport mechanism.

C. Natural Sources and Sinks of Ozone in the Troposphere

In the 1950s (Leighton, 1961; Wayne, 1962), it was shown that ozone synthesis was possible in polluted atmospheres. In 44 out of 251 cases, Hering and Borden (1967) found ozone concentration below 5 km to be greater than above 5 km. In seven of these cases, the O_3 concentration was greater at or below 2.5 km than at the tropopause. As argued by Kroening and Nye (1962), tropospheric layers of O_3 concentration near the tropopause can be explained by stratospheric intrusion, but high values near the ground can be more easily explained in terms of in-situ synthesis than in terms of subsidence, through half the troposphere, of a layer of high O_3 content.

As previously mentioned in Section I-A, Went (1960) suggested a photochemical mechanism for tropospheric ozone synthesis using natural terpenes and NO_2 . Ripperton et al. (1971) tested this hypothesis under controlled conditions and confirmed that this process can result in ozone formation similar to that occurring in polluted atmospheres. Rasmussen and Went (1965) found an average of 1 pphm (maximum of 5 pphm) of atmospheric terpenoid compounds in the Appalachian and Ozark Mountains. Lodge and Pate (1963) measured an average of 0.09 pphm NO_2 (maximum of 0.5 pphm) in Panama, and Worth et al., (1967) measured an average of 0.4 pphm NO_2 (maximum of 2.6 pphm) in the southern Appalachians. Thus it is clear that both natural terpenes and natural NO_2 are emitted in quantities significant enough to influence O_3 behavior.

Crutzen (1973) pointed out that the methane oxidation chain, which ultimately leads to the production of CO, represents a large source of

ozone. Chemides and Walker (1973) presented a photochemical theory of tropospheric ozone synthesis from the methane oxidation chain. Calculations indicate that this mechanism can support an ozone production rate of $5 \times 10^6 \text{ cm}^3/\text{s}$. Their calculations yield a photochemical lifetime of O_3 ranging from about one day at 5 km to about 10 days at 10 km. Since the mixing time due to the presence of eddies in the troposphere is about 30 days (Junge, 1962), this result suggests that O_3 is in photochemical equilibrium in the troposphere, contradicting the usual view of O_3 as a relatively inert constituent of tropospheric air.

The model of Chemides and Walker (1973) was found to satisfactorily explain the general variation of O_3 with season as well as its dependence on altitude. Indeed there is agreement that earlier assumptions that ozone is destroyed on heterogeneous surfaces only were incorrect and that gas phase ozone destruction is an effective sink for ozone (Ripperton and Vukovich, 1971). Lightning from thunderstorms may also cause local increases in ozone, but by itself this mechanism constitutes an insignificant ozone source in remote areas (Shalanta and Moore, 1972).

D. Long-Range Transport and the Nonurban Oxidant Problem

Most of the nonurban data taken before the mid-1960s consistently reports low ozone values all over the world. McKee (1961) reports a maximum ozone concentration of 0.013 ppm based on his measurements in Greenland. Junge (1963) summarizes a number of observations prior to 1961, with most of the concentrations being below 0.045 ppm (see Table 2). Only one location reports O_3 values as high as 0.06 ppm. In the Antarctic region, the mean surface ozone values ranged from 0.01 to 0.034 ppm, based on data from April 1957 to May 1958. At the Admundsen Scott Station located at the geographical South Pole monthly average mean values of 0.01 to 0.04 were obtained (Aldaz, 1967). During other studies conducted by the University of North Carolina during 1964 and

Table 2
COMPILATION OF REPRESENTATIVE OZONE CONCENTRATION NEAR THE
GROUND AND AT HIGHER LEVELS WITHIN THE TROPOSPHERE (Junge, 1963)

OBSERVER	LOCATION, TIME AND RESULTS	ALTITUDE (Meters)	OZONE CONCENTRATION $\mu\text{g}/\text{m}^3$ ^c	
			RANGE APPROXIMATE	AVERAGE APPROXIMATE
Gots & Vols (1951)	Arosa, Switzerland, 1950-51, high valley, daily maxima value	1860 m above sea level	19-90 daily maximum values	50
Ehmert (1952)	Weissenau, Bodensee, Germany, 1952	20 m above ground	0-90 all values	35 ^a
Kay (1953)	Farnborough, England, 1952-53	0-12000 m above ground	26-30 a few aircraft soundings	38 ^b
Regener (1954)	Mt. Capillo and Albuquerque, New Mexico, USA, 1951-52	3100 and 1600 m above sea level	3-120 all data	36 ^a
Regener (1954)	O'Neil, Nebraska, USA, 1953	12 m above ground	0-90 all data	35 ^a
Teichert (1955)	Lindenberg Observ., Germany, 1953-54	80 m above ground	0-50 all data	30 ^a
Breuer (1955)	Tromsø, Norway, 1954	0-10000 m above ground	60-70 a few air- craft sound- ings	65
Teichert & Warmbt (1956)	Fichtelberg, Central Germany, 1954-55	1215 m above sea level	20-67 monthly average values of hourly observa- tions	40
	Brocken, Central Germany, 1955	1152 m above sea level	26-52 monthly average values	40
	Kaltennordheim, Central Germany, 1955	494 m above sea level	15-25 monthly average values	20 ^a
	Wahnsdorf, near Dresden, East Germany, 1954-55	257 m above sea level	2-26 monthly average values of hourly observations	12 ^a
Price & Pales (1959, 1961)	Mauna Loa, Hawaii, 1958	3000 m above sea level	20-80 daily maxi- mum values	50
Wexler et al. (1960)	Little America Antarctica, 1958	50 m above sea level, near the ground	10-70 all values	50
Ramanathan et al. (1961)	Srinagar, North India, 1957-1960	1700 m above sea level	26-59 monthly average values of daily maxima	50
Dave (1961)	Ahmedabad, 1954-55	50 m above sea level, near the ground	24-50 monthly average values of daily maxima	40
^a Influence of ozone destruction near the ground not eliminated in these average values. To some extent this applies also to other sets of data, except for those which refer to daily maximum values. ^b Values likely too low due to ozone destruction in the intake tube. ^c To convert $\mu\text{g}/\text{m}^3$ to pphm, divide by 20.				

1967 in rural North Carolina, high ozone values were not observed (RTI, 1975).

However, as mentioned earlier, a study sponsored by EPA in 1970 in a rural area of western Maryland and eastern West Virginia, oxidant values well in excess of the NAAQS (0.08 ppm) were frequently measured (EPA, 1970; Richter, 1970), which led to a number of studies on the rural oxidant problem. In the summer of 1972, the EPA sponsored a special study for ozone measurements in Garret County, Maryland, and Preston County, West Virginia (EPA, 1972). Approximately 11 percent of the 1043 hourly measurements measured by the gas-phase chemiluminescent method exceeded 0.08 ppm. The maximum O_3 value during the study period (4 August to 25 September 1972) was 0.12 ppm. Simultaneous measurements of NO_x and nonmethane hydrocarbons (NMHC) concentrations yielded values that were at or near geochemical levels. Neither natural nor anthropogenic sources in the study area appeared capable of producing the required precursor species (HC and NO_x) in sufficient quantities for synthesis of ozone at the levels observed.

A more extensive study was conducted in the summer of 1973, when ground-level ozone was measured at McHenry, Maryland, Kane, Pennsylvania, Coshocton, Ohio, and Lewisburgh, West Virginia between 26 June and 30 September 1973. The measurement period at Kane extended through October. A C-45 aircraft equipped with a solid-phase chemiluminescent ozone meter was used to measure O_3 aloft. Hourly O_3 concentrations exceeded the NAAQS for oxidants 37, 30, 20 and 15 percent of the hours for which data were available at McHenry, Kane, Coshocton, and Lewisburgh, respectively. The aircraft data further indicated that the source of high O_3 was located at the surface, because vertical O_3 profiles showed a distinct concentration decrease with altitude. Maximum hourly ozone concentrations were 0.16 ppm at McHenry, 0.14 ppm at Kane, 0.17 ppm at Coshocton, and 0.13 ppm at Lewisburgh.

Miller et al. (1972) measured ozone at several rural and urban locations near Fresno, California during the period 17-27 August 1970, and found the NAAQS was widely exceeded. In the rural locations the 11-day average for each of the hours between 11 a.m. and 6 p.m. was in excess of 0.08 ppm, with the lowest hourly average about 0.05 ppm. High O_3 concentrations in rural areas were attributed to transport from the Fresno urban area; however, the authors were unable to explain why the O_3 concentration remained high when the prevailing wind was not from the direction of the city.

Since 1973, a great deal of emphasis has been placed on the non-urban problem. The oxidant conditions that had been typically observed in California were found to be quite widespread. Based on limited 1973 oxidant data in New York state, Stasiuk and Coffey (1974) concluded that, since average daily rural ozone concentrations at widely separated sites correlated well with the daily maximum urban ozone concentrations, a common source was implied. They discounted transport as the primary source of high nonurban oxidant values.

In another study, Cleveland et al. (1975) conducted an analysis of data from the New Jersey/Pennsylvania area and concluded that the oxidant problem in rural Ancora was caused by regional oxidant transport from the Philadelphia-Camden urban complex. These authors also observed that Sundays, with typically lower emissions, were overrepresented among the days that exceeded the NAAQS in New Jersey.

Wolff (1974), in a preliminary investigation of the tri-state (New York-New Jersey-Connecticut) photochemical oxidant problem, concluded that the NAAQS is widely exceeded in the tri-state region and suggested that this may be due to precursor transport from the Philadelphia-Camden area, especially with west or southwest winds. No correlation was found between the early morning (6 to 9 a.m.) hydrocarbons and the afternoon

ozone at any given station. High afternoon temperatures ($> 86^{\circ}\text{F}$) and a mixing depth of less than 500 m resulted in high O_3 concentrations. Wolff also observed high O_3 concentrations associated with the sea-breeze cycle, and proposed a hypothesis similar to the one suggested by Lyons and Cole (1974).

Lyons and Cole observed very high oxidant values in 1973 in southern Wisconsin rural areas and along the shoreline of Lake Michigan. Rural hourly ozone values as high as 0.2-0.3 ppm were measured several times. The results of this study indicated that significant mesoscale and even synoptic-scale transport of ozone into this particular area might occur.

Several other studies conducted in California (Cavanagh and Smith, 1973; Blumenthal et al., 1974) confirmed large-scale transport of ozone and ozone precursors. In Los Angeles, it was found that the urban plume may extend as much as 70 to 100 miles downwind of the city. Studies at Houston and Phoenix (Rasmussen et al., 1974) and Philadelphia (Cleveland, 1975) confirmed that transport from urban centers as far as 30-50 miles downwind is quite widespread.

Extensive oxidant monitoring in rural areas was conducted in 1974. Perhaps the most comprehensive single study to date on urban/nonurban oxidant interrelationships was conducted in the Ohio Valley in the summer of 1974. It was concluded that oxidant values in the rural areas clearly exceeded the NAAQS. After about 30 to 50 miles, a single urban plume was found to lose its identity (RTI, 1975). It was also found that a distinct and nearly identical diurnal ozone variation at widely separated locations indicated that area-wide mixing processes were important. Specific air trajectories could not be consistently associated with the arrival of air containing high or low oxidant values. It was found that high oxidant values persisted with the incoming movement of high pressure systems. Martinez (1975), in reviewing the relation of

oxidant values with meteorological features, found that high rural oxidant values appear to be related to the influence of high pressure cells, maximum temperatures above 60°F, abundant sunshine, low wind velocities, and low-level atmospheric instability.

On the basis of the Ohio studies, Ripperton et al. (1974) support the surface origin of high oxidant values and discount the possibility of significant stratospheric transport. Rasmussen and Robinson (1975) present a qualitative surface ozone model which describes the approximate oxidant contributions to be expected in rural and urban locations from both natural and anthropogenic sources.

Other studies in the New York-New Jersey-Connecticut area have attempted to relate the high east coast rural oxidant values to various meteorological factors (Graedel et al., 1974). Bruntz et al. (1974) have attempted to obtain an empirical correlation between O_3 , solar radiation, wind speed, and air temperature by using statistical curve-fitting methods. Cleveland et al. (1975) explain that the high nighttime ozone values in Massachusetts are indicative of transport from the New York-Connecticut area. Coffey and Stasiuk (1975) propose that the high nonurban ozone concentrations would result in a reverse transport to urban areas, making any urban oxidant controls ineffective. Rubino et al. (1975) report high urban and nonurban O_3 values in Connecticut, and attribute this to transport from New York City.

In the Houston area, the Goober III study (Fowler et al. 1975) confirmed that oxidant was transported from Houston to a nonurban site in Prairie View (40 miles northwest of Houston). However, during the Yellow Pine study conducted during April-June 1974 in eastern Texas, no evidence of transport could be found. The measured ozone concentrations showed a diurnal profile, with peak O_3 concentrations in the early afternoon. The NAAQS was exceeded only twice during the monitoring period.

Becker (1974) analyzed data from the Wisconsin area, where O_3 was monitored at seven urban and four nonurban locations. The rural sites in southern Wisconsin were found to experience more hours of alert levels (400 ppb) than the four urban Milwaukee sites.

Based on his ozone measurements in Miami, Florida, Nagler (1974) confirmed the high O_3 levels on an area-wide basis, with indications of long-range transport from the Chicago-Pittsburgh urban complex (Fankhauser, 1975).

In Beulah, North Dakota, a relatively remote location, it was found that 23 percent of all one-hourly average concentrations exceeded the NAAQS, based on a brief sampling study in July 1974. Values as high as 0.12 ppm were measured and no evidence of transport was found. It was suggested that scarcity of foliage in the area with which O_3 might react could account in part for the high ozone values (Browning, 1975).

In a modeling study based on measurements from the Ohio Valley and Los Angeles, Johnson and Singh (1975) examined the significance of O_3 in the upper inversion layer in terms of its effects on concentrations at the surface level. They found that high night time ozone values and the "weekend effect" could be explained by ozone layers aloft dispersing downwards during turbulent conditions. This phenomenon is expected to be significant in both urban and rural locations. It may be especially significant in nonurban areas because of the lack of primary ozone-destroying precursors.

Among the locations that showed low oxidant values were monitoring sites in Wyoming and Montana. At the Powder River Plant in northwest Wyoming, ozone data taken from 1 January to 30 June 1974 yielded values that were typically between 0.03 and 0.05 ppm (Ancell, 1975). The maximum hourly concentration measured was 0.071 ppm. At McRae, Montana (Tsao, 1974), O_3 was monitored from December 1973 to June 1974 with a

total of 3820 hourly values obtained over a period of 184 days. At no time did the maximum O_3 value exceed the NAAQS. A vast majority of the data was below 0.06 ppm.

It is obvious, therefore, that effective control strategies cannot be formulated until there is general agreement on some of the basic questions. Altshuller (1975) has attempted to delineate some of the important questions that must be answered. He concludes that the effects of downwind transport and the growth of suburban cities must be isolated. He also points to a scenario that may apply on the east coast area, in which urban plumes constantly intermix with naturally emitted precursors as well as with other plumes.

The question of what is a natural ozone background is also a confusing one, since recent data seem inconsistent with measurements made a few years ago. While it is not possible to completely define the accuracy of data taken before the mid-1960s, it is difficult to make a strong argument that the earlier data are wrong (RTI, 1975). However, even today there is considerable controversy about ozone measurement methods, and the possibility that all EPA measurements are 22 percent too high (Demore et al., 1975) would imply that the nonurban problem is probably less serious than hitherto believed.

Vertical ozone profiles showing a characteristic decline with height have been used as the primary argument in favor of the surface origin of ozone in rural areas (RTI, 1975). However, high concentrations of ozone aloft at these same rural areas are found trapped within inversion layers (Johnson and Singh, 1975).

As more data become available it should be possible to develop a consensus on what is a typical background ozone level, what is the nature and extent of urban transport, and what strategies must be used to control the oxidant problem. If trajectory analyses cannot define

consistent source-receptor relationships, and if area-wide effects are shown to be prevalent, regional strategies will have to be developed.

E. Summary of Significant Scientific Findings

As has been discussed in this section, a number of intensive studies have been made on the urban/nonurban oxidant relationship, and a wealth of data are at hand. In addition, a number of monitoring stations over the continental United States have helped generate an extensive data base for both urban and nonurban locations. Although considerable disagreement still persists on various points, a number of findings have been generally confirmed by these efforts, and are summarized below:

- Urban oxidants are directly attributable to precursor emissions and their relationships (HC, NO_x, HC/NO_x) in urban areas.
- Oxidant levels are generally higher in those suburban areas that are located directly downwind from central urban locations.
- In the absence of NO, the sinks for oxidant such as NO₂, olefins, particulate matter, and surface features scavenge ozone slowly. However, urban plumes can affect oxidant levels at a range exceeding 50 miles.
- Oxidant aloft may be effectively isolated from destructive precursors and can be entrapped within stable inversion layers. This oxidant can diffuse downward either during the following day or at night if turbulent conditions persist. The persistence of oxidant in layers aloft and its downward diffusion occurs in nonurban as well as urban locations.
- While short-range horizontal transport of oxidant and oxidant precursors has been generally invoked as the cause of high oxidant levels, recent investigations indicate mesoscale and even synoptic-scale transport of oxidant over the United States. Distances of travel, persistence of oxidant and oxidant precursors, and the contributions of large and small sources superimposed on large-scale transport have prevented the identification of clear cut source-receptor relationships by

trajectory analysis. An analysis of nonurban hydrocarbon data, even though limited, suggests that nonurban hydrocarbons are composed of the same complex mixtures that characterize urban areas. Similar oxidant diurnal variations are also observed in both urban and nonurban areas.

- Lightning from thunderstorms may cause brief local increases in ozone but by itself constitutes an insignificant source of ozone.
- Ozone contributions from natural precursors and stratospheric ozone injections are likely to be between 0.04 and 0.05 ppm. Ozone from natural hydrocarbons may increase the ambient ozone by 0.02 to 0.05 ppm, however the atmospheric conditions that are conducive to ozone production from photochemical processes are usually different from conditions that favor transport from the stratosphere.
- Typically, high temperatures ($> 60^{\circ}\text{F}$), abundant solar flux, low wind speeds, high pressure cells and low-level instability present favorable conditions for elevated oxidant levels. A fairly good statistical correlation exists between oxidant levels and temperature, relative humidity, and inverse mixing height.
- Synoptic-scale weather patterns with migratory anticyclones achieve a widespread mass of air contamination.
- High pressure cells often have the highest oxidant concentrations near the center of the cell in an area of about 100 to 200 miles in diameter, where conditions are apparently conducive to high oxidant formation.
- More recent results favor the area-wide mixing hypothesis, in which natural precursors constantly intermix with urban plumes. So far, trajectory analysis has not been useful to relate high or low rural oxidant concentrations to any specific sources. A significant possibility is the transport of hydrocarbon precursors of lower reactivities from urban locations over long distances, which then intermix with NO_x from both natural and anthropogenic sources to form high oxidant concentrations in rural areas.
- For a long time the belief has been that oxidants were formed from reactive hydrocarbons such as olefins, some aromatics and aldehydes only, and nonreactive hydrocarbons

which were a significant portion of the hydrocarbons emitted, did not contribute to oxidant formation. It has now become clear that all hydrocarbons (even methane) are capable of forming oxidants and the only real difference is the relative time of irradiation. Thus very low reactivity hydrocarbons (say alkanes) will eventually lead to ozone formation but the chemical processes may take several days. Such occurrences will lead to a higher background of ozone, and long-range transport of hydrocarbons and thereby of oxidants.

III DESCRIPTION OF SELECTED RESEARCH STUDIES

In this section we present brief summaries of the results of a selected number of research studies that are judged to be significant in terms of the relation of oxidant levels to meteorological features. Both theoretical studies and observational studies that contain analyses of data are included. With regard to observational studies, the emphasis in this review has been placed on the results of analyses of oxidant or ozone data collected in the United States east of a line from the western border of the Dakotas southward to El Paso, Texas. However, a few studies elsewhere that contain results of apparent general significance have also been included. The summaries are presented in alphabetical order, by author.

(1) Flux Measurements of Atmospheric Ozone over Land and Water
(Aldaz, 1969)

Based on experimental measurements, it is estimated that ozone destruction rates are $0.60 \text{ cm s}^{-1} (\text{cm}^3 \text{ cm}^{-2} \text{ s}^{-1})$ over land, 0.04 cm/s over fresh water, and 0.02 cm/s over the ocean. Assuming a destruction rate of ozone by tropical vegetation that may vary from 0.06 cm/s to 3.0 cm/s , it is estimated that global sinks for ozone vary from 5.4 to $8.6 \times 10^{29} \text{ molecules s}^{-1}$ (or 1.3 to 2.1×10^9 tons of ozone per year). Because of the land-sea distributions of the northern and southern hemisphere, the southern hemisphere is estimated to account for 1.5 to $3.1 \times 10^{29} \text{ molecules s}^{-1}$. The ozone density is taken to vary from 35 to $55 \text{ } \mu\text{g/m}^3$, depending on latitude.

(2) Evaluation of Oxidant Results at CAMP sites in the United States
(Altshuller, 1975)

Oxidant measurements available between 1964 and 1973 at six CAMP sites (Chicago, Cincinnati, Denver, Philadelphia, St. Louis, and Washington, D.C.) were evaluated. Elevated oxidant concentrations were characterized by season, hour of the day, Sundays compared to weekdays, sampling site, and long-term trend. With the exception of Chicago, downward oxidant trends are reported at all CAMP sites. These and other studies indicate that proportional declines in suburban locations have not been achieved. It is concluded that effects of downwind urban transport cannot be isolated from the growth of suburban cities. The paper points to the significance of urban plumes that extend 50 to 100 miles downwind, constantly intermixing with natural emissions as well as with other urban plumes. If long-range transport is indeed important, regional scale strategies will be required. It has been generally observed at CAMP sites that a general downwind shift in HC/NO_x ratios is occurring. This could also explain the greater linear decrease in oxidants, compared with the nonmethane hydrocarbons.

(3) Mesoscale Flows and Ozone Levels in a Rural California Coastal Valley (Baboolal, 1975)

The mesoscale flow over a rural California coastal valley is characterized using year-long data collected by a network of field sites made up of surface winds, acoustic radar, sigma meter, and temperature soundings. With the additional support of the historical meteorological data the air pollution is defined. The presence of well-developed drainage flows with noticeable turbulence appears on the acoustic radar record; this is supported by the sigma meter turbulence measurements. Three times daily, temperature profiles, taken at increasingly greater distances from the Pacific Coast, were used to characterize the inversion climatology of the marine layer. Simultaneous ozone soundings reveal unusually high levels aloft, suggesting the rural valley itself to be the unlikely source. This suggestion is supported by the results of a limited modeling effort.

(4) Three-Dimensional Pollutant Gradient Study--1972-1973 Program
(Blumenthal et al., 1974)

Two years of data on the 3-D distribution and transport of aerosols and gaseous pollutants in the South Coast (Los Angeles), San Joaquin Valley, and San Francisco Bay air basins were obtained and analyzed. Two hundred forty sampling flights on 59 different days were made by two aircraft in conjunction with ground-level sampling. Extensive meteorological data were obtained along with the scattering coefficient, condensation nuclei, O_3 , NO_x , CO, turbulence, temperature, and humidity data obtained by the aircraft.

The data present a detailed picture of the mixing layer structure and ventilation processes in the Los Angeles Basin and point out the modifications to the normal mixing and ventilation processes that lead to episode conditions. The air pollution problem in Los Angeles and other air basins is shown to be a regional problem exemplified by the accumulation of pollutants in a stagnant air mass and subsequent transport to downwind areas. Various statistical and other analyses were performed on the data, which demonstrated the changes in the aerosol and gaseous pollutants as they aged and indicated certain factors contributing to aerosol formation and growth.

Other special studies were performed, which documented in some detail the structure of a few point source plumes and demonstrated the possible buoyant effect of roadways. A 24-hour sampling program in the eastern Los Angeles Basin documented the overnight stability of ozone at high concentrations in aged polluted air.

(5) Some Large-Scale Features of the Vertical Distribution of Atmospheric Ozone Associated with the Thermal Structure of the Atmosphere (Breiland, 1968)

Ten-case running means of the vertical distributions of hydrostatic stability and of the vertical fractional gradient of the partial pressure of ozone computed from ozone and temperature soundings arranged according to tropopause height are presented for four stations located in different latitudes. It is shown that the characteristic large-scale features of the vertical distributions of the vertical ozone gradient correspond closely to similar characteristic large-scale features of the thermal structure of the atmosphere depicted by the vertical distributions of the hydrostatic stability. The layer structure of the ozone gradient and of the hydrostatic stability both show characteristic features that vary significantly with latitude and with the height of the tropopause.

(6) The Dependence of Ambient Ozone on Solar Radiation, Wind Temperature, and Mixing Height (Bruntz et al., 1974)

Based on physical theory and "weathervane plots" of data collected from New York metropolitan area, the authors conclude that O_3 concentrations are statistically related to wind speed, solar radiations, and air temperature. They obtain the following equation using statistical curve-fitting methods, and claim a correlation coefficient of 0.84 between the observations and the predicted values:

$$O_t = 3.29 (\pm 0.70) + 0.21 (\pm 0.04) \log_{10} S - 0.61 (\pm 0.11) \log_{10} V \\ + 2.65 (\pm 0.36) \log_{10} T$$

where

$$O_t = \log_{10} [O_3(\text{ppb}) + 5]$$

S = solar radiation (Langleys)

V = wind speed (mi hr^{-1})

T = air temperature (deg F)

(7) The Transport of Photochemical Air Pollution From the
Camden-Philadelphia Urban Complex (Cleveland and Kleiner, 1975)

This paper reports the results of an analysis of ground-level hourly chemiluminescent ozone measurements obtained from 1 May 1973 to 30 September 1973 and from 1 May 1974 to 13 September 1974 from four stations surrounding the Philadelphia-Camden urban complex. With the aid of a graphical-statistical technique, it is shown that at each of four sites in New Jersey and Pennsylvania, ranging from 27 km to 49 km away from the center of the Camden-Philadelphia urban area, ozone concentrations are higher when the air is flowing from the urban area to the site. It is judged by the authors that this accounts for some of the ozone previously observed in the nonindustrial, low-traffic-density area of Ancora, New Jersey, where concentrations of primary pollutants are low, but where ozone daily maxima frequently exceed the federal standard. It is thus concluded that photochemical air pollution in this area is a regional rather than a local phenomenon, and ozone resulting from emissions from the urban area is widespread and not confined to the urban area itself.

- (8) The Analysis of Ground-Level Ozone Data from New Jersey, New York, Connecticut, and Massachusetts: Data Quality Assessment and Temporal and Geographical Properties (Cleveland et al., 1975)

Hourly ground-level ozone measurements from 41 sites in eastern New York, northern New Jersey, Connecticut, and Massachusetts from 1 May 1974 to 30 September 1974 were analyzed. Various techniques for assessing data quality and uniform calibrations show the data to be of high reliability for yielding information on the ozone problem in the region. Nighttime concentrations, relative to those during the day, are highest in Massachusetts; more specifically, the ratio of the upper quartile of hourly average ozone concentrations at 1500 hours EST to the upper quartile at 0100 hours EST decreases with increasing distance from New York City, which is in the center of the tri-state urban complex (northern New Jersey, southwestern Connecticut and New York City). The site distributions of daily maximum concentrations are highest in the Stamford-Greenwich region of Connecticut and next highest in a region to the east and northeast of Stamford-Greenwich. The lowest O_3 concentrations were found in Boston, Waltham, Springfield, Newark and Elizabeth; however, all five stations were located next to automobile emission sources and the NO emissions could account for the low oxidant levels measured at these poorly located sites.

(9) Long-Range Transport of Photochemical Ozone in Northwestern Europe (Cox et al., 1975)

Measurements of the concentrations of ozone and trichlorofluoromethane in the atmosphere were obtained in 1973 at three locations in the southern British Isles. The U.S. Air Quality Standard for photochemical oxidants was exceeded on a number of days at all three sampling sites, including one situated in southern Ireland. The authors conclude that in suitable meteorological conditions, measurable amounts of photochemical pollution of anthropogenic origin are transported over distances up to at least 1,000 km in northwestern Europe, and that occasionally continental emissions provide a major contribution to photochemical pollution in the United Kingdom. During such periods photochemical pollution is essentially a regional rather than a local problem, with uniformly elevated concentrations of photochemical ozone being observed simultaneously over different parts of the United Kingdom. It follows that, should controls on the emission of the pollutant precursors (hydrocarbons and nitrogen oxides) be considered necessary to reduce future levels of photochemical oxidants in the United Kingdom, then such controls are unlikely to be effective in the absence of similar controls elsewhere in Europe.

(10) Vertical Distribution of Photochemical Smog in Los Angeles Basin (Edinger, 1973)

Aircraft soundings of oxidant concentration and temperature in the vertical section from the Santa Monica coastline inland to the San Bernardino area were analyzed. In addition to the polluted layer confined beneath the temperature inversion, laminae of pollution were detected within the inversion layer with concentrations of oxidant as high as those observed in the ground-based smog layer. It is hypothesized that the upper layers of pollution are formed when a portion of the smog moving up the heated mountain slopes that bound the basin on the north moves out horizontally from the slopes at elevations between the top and bottom of the inversion.

(11) Penetration and Duration of Oxidant Air Pollution in the South Coast Air Basin of California (Edinger et al., 1972)

On June 18, 19, and 20, 1970, two aircraft, a rawinsonde, two pibal stations, and four ground stations provided simultaneous samples of total oxidant, temperature, and winds up to 8000 ft in an area extending from Santa Monica, Calif., east to Redlands and north across the San Bernardino Mountains. It was shown that photochemical oxidant formed in the marine layer is vented up the slopes and over the crest of the San Bernardino Mountains during the day. Layers of high oxidant concentrations were detected above the inversion base, suggesting that some pollution is vented up the slopes and subsequently advected back to the south. The diurnal changes in the temperature inversion also contribute to the high concentration found above the inversion base. These processes result in multi-layers of pollution. The study suggests that oxidant air pollution is transported up to 80 mi to forested mountains, where severe damage to conifer species has been documented.

(12) Control of Photochemical Oxidants--Technical Basis and Implications of Recent Findings (EPA, 1975)

To insure the technical accuracy of the oxidant control strategy and to refine that strategy where necessary, EPA has conducted a continuing program of research studies and data analysis. New findings based on laboratory and field studies accomplished over the last several years generally support the control measures currently being taken and further indicate that additional measures may be necessary to meet the oxidant standard nationwide. These recent studies have documented frequent violations of the oxidant standard in both urban and rural areas although, in some urban areas, both the maximum concentrations of oxidants and the frequency of violations have decreased over the past several years. At rural locations, the number of violations of the standard and the maximum concentrations are sometimes as high and even higher than in nearby urban areas. It is thus apparent that oxidants are a rural as well as an urban problem.

The recent studies show that: (1) man-made emissions are the predominant source of high levels of oxidants, even in remote rural areas; (2) the contribution of natural sources of oxidants is usually not more than 0.05 ppm, compared with the oxidant standard of 0.08 ppm; and (3) transport of oxidants and their precursor compounds has been demonstrated to about 50 miles downwind of urban areas and it is likely that transport over longer distances occurs. It also has been shown that the highest oxidant concentrations in the Midwest in both rural and urban areas occur during periods of stagnant conditions associated with high pressure weather systems.

In both urban areas and in many nonurban areas, there appear to be sufficient emissions of man-made precursors to account for the high oxidant levels observed. While transport of oxidants and their precursors may occur, most urban areas probably are responsible for their own

oxidant problem. The high oxidant levels in nonurban areas appear to be the result of both locally produced precursors and precursors transported from urban and other nonurban sources. As a result, control strategies for nonurban areas will need to be directed at measures which reduce emissions from both nonurban sources as well as urban sources and which meet the specific needs of each of these areas.

The following implications of the new findings are suggested:

- Because of the high precursor emission densities and the large numbers of people exposed to oxidants, continued emphasis on intensive control measures within cities will be necessary to meet the oxidant standard in major urban areas.
- It may be necessary to extend some measures under present state implementation plans to include nonurban areas as well as cities.
- Although mobile source controls (including transportation control plans) will continue to be a major part of the oxidant control program, there is a need for more stringent control of precursor emissions from stationary sources.
- Both under conditions of transport and under persistence of stagnant air masses there can be sufficient time for less reactive hydrocarbons to contribute to oxidant formation. This indicates the importance of controlling all organic compounds that can form oxidants.
- Nitrogen oxides emissions may be transported into rural areas and contribute to oxidant formation by reaction with locally emitted organic compounds. It may eventually become necessary to consider control of nitrogen oxides, coordinated with the control of hydrocarbons, as a part of the oxidant control strategy.
- Oxidant concentrations that can be attributed to natural sources are usually less than 0.55 parts per million compared with the oxidant standard of 0.08 parts per million. Because of emissions from natural sources, more stringent reductions of man-made emissions may be necessary in some areas.

- (13) A Theoretical Investigation of Tropospheric Ozone and Stratospheric-Tropospheric Exchange Processes (Fabian, 1973)

Based on the global distribution of various surface types the mean tropospheric residence time of ozone is estimated as a function of latitude. Due to the land-sea distribution it varies from 50 days in the northern hemisphere to 190 days in the southern hemisphere. For the stratospheric-tropospheric exchange a sinusoidal variation with season is assumed. The annual variation of tropospheric ozone thus gets a sine function from mean, amplitude, and phase from which the injection function for the particular latitude can be determined. Ozone and strontium-90 fallout data show similar behavior between 25° south and 65° north latitudes.

- (14) Ozonesonde Observations over North America, Vols. 1-4 (Hering and Borden, 1964a, 1964b, 1965b, 1967)

An experimental program for the measurement of the vertical ozone distribution was established by the Air Force Cambridge Research Laboratories (AFCLR) in January 1963. Observations from eleven network stations spread throughout North America have been published in this series of four reports. Ozonagrams for individual ozonesonde ascents made during the period January 1963 to January 1966 are included.

The fourth volume also presents a statistical summary of the ozonesonde data for the three-year period ending December 1965. Seasonal mean ozone profiles and the standard deviations from the average distributions are given for each station. Correlations of the ozone concentration at specific levels with temperature, pressure, and total ozone are also summarized.

(15) Mean Distribution of Ozone Density over North America, 1963-1964
(Hering and Borden, 1965)

An interim summary of the ozone climate over North America was prepared from AFCRL ozonesonde network observations made during 1963 and 1964. Mean bimonthly distributions of ozone density computed for individual network stations depict the average ozone structure as a function of altitude and season for the first two years of network operation. Data are also presented on the standard deviation of ozone density and the mean seasonal distributions along a meridional cross section extending from the Canal Zone to Greenland. A brief statistical analysis indicates that approximately 35 to 50 percent of the variance in the total ozone amount at middle and high latitudes is given by the fluctuations in ozone density in the 11- to 13-km or 13- to 15-km layers.

(16) Photochemical Oxidants in the New York-New Jersey Metropolitan Area (Jacobson and Salottola, 1975)

Atmospheric oxidant concentrations measured at seven locations during the years 1970-1972 were compared to explore the nature of the photochemical oxidant problem in the New York-New Jersey metropolitan area. The results indicate that oxidants occurred in highest concentrations during the months of May-September; a diurnal pattern existed during the spring and summer seasons with concentrations usually rising to a maximum between 12:00 and 17:00h Eastern Standard Time; the federal ambient air quality standard of 0.08 ppm was exceeded each year with a frequency varying with location; maximum hourly average concentrations for the region were in the range of 0.2-0.3 ppm; sites located in heavily trafficked areas generally reported lower oxidant concentrations than sites in suburban areas.

Comparisons between oxidants at Yonkers, a suburban location north of the metropolitan area, and meteorological measurements indicated that elevated concentrations occurred more frequently with wind directions from the southeast through southwest sectors, wind speeds between 6 and 11 miles h^{-1} , solar radiation intensities above 400 Langley, temperatures greater than 75°F, and with early morning mixing depths less than 1000 m. Concentrations of oxidants in Yonkers rarely exceeded 0.05 ppm during the winter or on days with low solar radiation.

It is concluded that during the spring and summer in the metropolitan area oxidant concentrations exceed federal standards more frequently than any other pollutant, that oxidants are formed largely by photochemical reactions as polluted air is transported from urban to suburban areas, that elevated oxidant concentrations occur more frequently at less urbanized locations downwind of major sources of emissions, and that concentrations which reach or exceed the ambient air quality standard arise mainly from

pollutant emissions occurring in the heavily urbanized portion of the metropolitan area while natural sources of oxidants and their precursors make less significant contributions to the photochemical oxidant problem in this region.

The oxidant measurement methods employed either colorometric (Beckman or Technicon) or coulometric (Mast) analyzers. The standard calibration method (neutral buffered KI) was used throughout. At the Yonkers station during the summer of 1973, chemiluminescent measurements of ozone and coulometric oxidant measurements gave comparable results.

(17) Surface Ozone in the Arctic Atmosphere (Kelly, 1973)

Near-surface atmospheric ozone measurements were carried out at Barrow, Alaska ($71^{\circ} 19'N$, $156^{\circ}W$), from January 1965 to September 1967. Ozone was continuously monitored by microcoulombmetric analysis at a level 2 m above the ground. Daily ozone concentrations near the ground varied from 7 to less than 1 pphm by volume. Highest concentrations occurred in the spring and showed sharp increases lasting from several hours to a few days. These sudden rises in ozone concentration correlated with storm front passages. The concentration of surface ozone from late spring through the summer and fall showed less variability from day to day than in the spring. The lowest ozone concentrations occurred from late May to early June.

(18) The Vertical Distribution of Ozone Over the San Francisco Bay Area (Lovill and Miller, 1968)

Observations of the vertical distribution of ozone were made during February 1967 in the San Francisco Bay Area with the carbon-iodine (Komhyr) ozonesonde. Horizontal and vertical velocity components were obtained by simultaneous tracking with an M33 radar. In the lower troposphere, two peaks of ozone were found near 1 and 1.5 km within the west coast subsidence inversion; the lower maximum coincides in position with a wind jet. In the middle and upper troposphere there are significant time variations of ozone, believed to be caused by intrusions of stratospheric air. Undulations in the ozone, temperature, and wind profiles in the stratosphere suggest laminae of air masses. The mean profile of ozone suggests that there are several distinct zones that are related to ozone production and vertical mixing.

- (19) The Use of Monitoring Network and ERTS-1 Data to Study Interregional Pollution Transport of Ozone in the Gary-Chicago-Milwaukee Corridor (Lyons and Cole, 1974)

Limited ozone monitoring conducted by EPA in Milwaukee during the summer of 1971 revealed surprisingly high values (5 episode alert levels in 99 days). In the summer of 1973, the Wisconsin Department of Natural Resources began installation of nine air quality monitoring stations in southeast Wisconsin, and one in rural Poynette (32 km north of Madison). The southeastern sites again revealed high values, two or more sites exceeding 8 pphm on 27 days over a 47-day period, with alert levels (40 pphm) being reached 9 times. Peak values between 20-30 pphm were recorded several times, especially at Racine, Wisconsin. Poynette also frequently exceeded 8 pphm.

An analysis of the data revealed several interesting facts. The winds were from the southwest through east-southeast fully 92 percent of the days during which the primary oxidant standard was exceeded. The data show that O_3 levels are comparatively low within 1 km of the shoreline and reach their highest values 1-4 km inland. This is confirmed by extensive bioindicator monitoring conducted in Milwaukee in 1972. A mechanism is proposed that illustrates how the complex wind and thermal structures in lake breezes could lead to continuous fumigation of stored oxidants to the surface in a narrow band parallel to the shore. Simply stated, oxidants are conserved over the lake area (in the absence of NO fluxes) and returned to the shore during the lake-breeze cycle in the morning.

In addition, the unexpectedly high values found both along the shoreline and at rural Poynette suggest that oxidants can be subjected to significant mesoscale and even synoptic scale transport. An ERTS image of the Lake Michigan area strongly supports a theory that much of the oxidants and/or its predecessor HC and NO_x originates in the Chicago-Gary area and is funneled northwards in the lake-breeze convergence zone.

It even seems conceivable that the high Poynette readings are the result of transport from such areas as St. Louis, Kansas City, Dallas, etc.

The low level nocturnal jet stream of the Great Plains is suggested as a plausible mechanism.

(20) Temporal-Spatial Variations of Nonurban Ozone Concentrations and Related Meteorological Factors (Martínez, 1975)

This paper provides a history of the nonurban ozone problem and summarizes the results of various studies that have been conducted since 1970. The primary information for the paper came from EPA-sponsored studies the eastern U.S. in 1972-1973 (Figure 6) and the summer of 1974 (Figure 7). These studies have revealed considerable temporal and spatial variations in ozone concentrations, with levels sometimes exceeding the national one-hour average ambient standard of $160 \mu\text{g}/\text{m}^3$ (0.08 ppm).

Both local and synoptic scale meteorological factors, including the role of transport from urban areas, have been examined and apparent relationships with ozone concentrations are described. A consistent statistical correlation was found between air temperatures in excess of 60°F and ozone concentrations in excess of the NAAQS. Trajectory analyses were inconclusive and showed no direct urban/nonurban pathway pattern. However, high O_3 values were associated with slower air movement. Further, synoptic weather features were found to correlate with ozone variations. Some high-pressure cells have maximum ozone concentrations at the center of the high. A slow-moving high pressure system is expected to be particularly conducive to high ozone values.



SA-4432-B

FIGURE 6 NONURBAN OZONE GROUND SAMPLING STATIONS, 1972-73 EPA-SPONSORED STUDIES (McHENRY ONLY 1972 SITE)

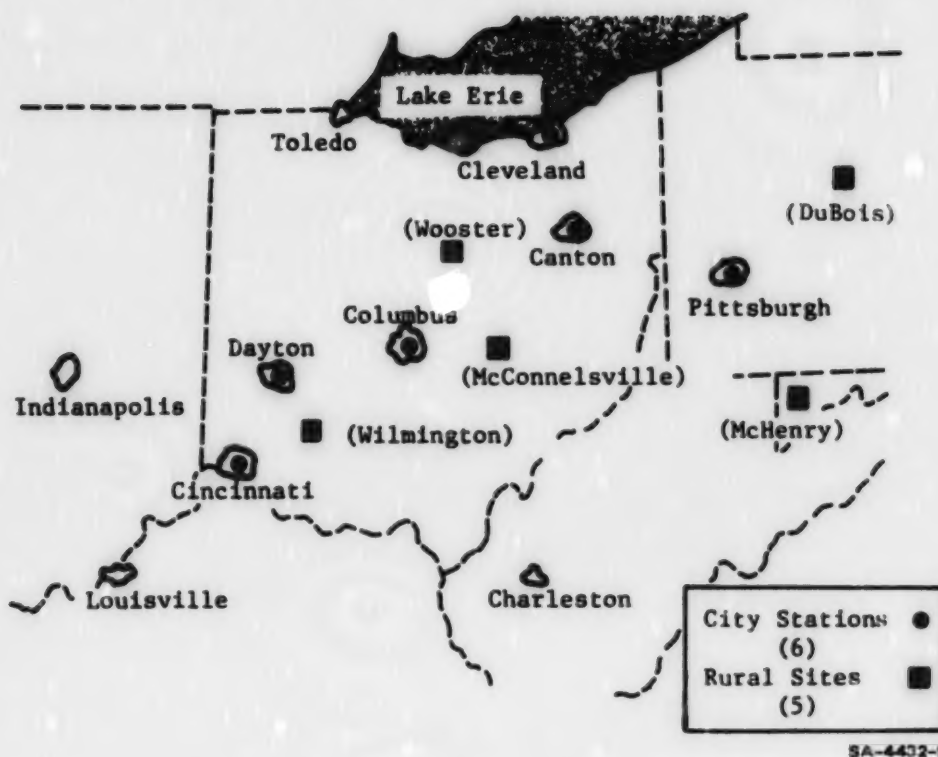


FIGURE 7 OZONE GROUND SAMPLING STATIONS, 1974 EPA-SPONSORED STUDY

(21) Ozone Within and Below the West Coast Temperature Inversion
(Miller and Ahrens, 1970)

The oxidant concentration in the air over the San Francisco Bay Area and the Pacific Ocean was measured up to an altitude of 2500 m and the observed distribution in the vertical and horizontal has been related to the characteristics and behavior of the west coast temperature inversion. Vertical time sections at fixed points and vertical cross sections were constructed of oxidant concentration, temperature, humidity, and winds measured from aircraft and radar.

The oxidant concentration in polluted air is strongly dependent on the destruction rate. The mean destruction rate within the surface layer depends directly on the intensity of eddy mixing and inversely on the square of the depth of the vertical mixing. Thus, the existence of a temperature inversion does not necessarily lead to a high concentration of oxidants, since the destruction rate may be high in a shallow mixing layer. The highest oxidant concentration was observed almost invariably at the edges of the west coast marine inversion, where pollutants are available for ozone production and the mixing layer is deep. Explanations are offered for the maxima of ozone that often occur above the inversion base. Distribution patterns of oxidants clearly depict the waving of the inversion layer.

(22) Oxidant Air Pollution in the Central Valley, Sierra Nevada Foothills,
and Mineral King Valley of California (Miller et al., 1972)

Total oxidant air pollution, temperature, and winds were measured in the Central Valley, the Sierra Nevada foothills, and Mineral King Valley from 17-28 August 1970. Vertical profiles of total oxidant and temperature were determined by aircraft (at Fresno, Visalia, Three Rivers and Mineral King) several times daily during a 2-day period. Evidence was recorded of the transport of photochemical smog from the Central Valley to Mineral King. In situ formation of oxidant and diurnal changes in the temperature profile in Mineral King Valley were observed.

(23) The Average Tropospheric Ozone Content and Its Variation with Season and Latitude as a Result of the Global Ozone Circulation (Pruchniewicz, 1973)

Evaluations of radiosonde soundings over North America and Europe, measurements aboard commercial airlines, and permanent ozone registrations at nineteen ground-based stations between Tromso, Norway, and Hermanus, South Africa, yield three belts of higher ozone intrusion from the stratosphere and maximum values of the annual means at about 30°N , and between 40° - 45°N and at about 60°N . A marked decrease of the annual mean values of the tropospheric ozone is detected towards the equator and the pole, respectively.

In the northern hemisphere the maximum of the annual cycle of the tropospheric ozone concentration occurs in spring at high latitudes and in summer at mid-latitudes.

For the tropical region from 30°S to 30°N a strong asymmetry of the northern and southern hemisphere occurs. This fact is discussed in detail. The higher troposphere of the tropics seems to be a well-mixed reservoir and mainly supplied with ozone from the tropopause gap region in the northern hemisphere. The ozone distribution in the lower troposphere of the whole tropics seems to be controlled by the up and down movements of the Hadley cell. The features of large-scale and seasonal variation of tropospheric ozone are discussed in connection with the ozone circulation in the stratosphere, the dynamic processes near the tropopause and the destruction rate at the earth's surface.

(24) The Role of Trace Atmospheric Constituents in a Surface Ozone Model
(Rasmussen and Robinson, 1975)

The authors present a description of a qualitative model of ground level ozone concentrations obtained by the chemiluminescent methods during several field studies conducted during 1973 and 1974. The model considers a typical rural site upwind and downwind of an urban site. The following features characterize model:

- Stratospheric ozone transport contributes about 30 to 50 ppb to the ozone concentration at ground level.
- Natural photochemical reactions (between terpenes and biogenic NO) contribute about 20 ppb to the natural background.
- Out of this total of 50 to 70 ppb of natural ozone, at least 10 ppb is lost due to reactions involving surface O_3 background level is about 40 to 60 ppb.
- As this air enters an urban location, the O_3 value quickly approaches zero because of reactions with urban NO and aerosols. The urban precursors (HC and NO_x) can photolyze to produce as much as 50 ppb of photochemical ozone.
- Urban ozone is then advected to downwind rural sites, while slow dispersive and destructive processes reduce this ozone level to near background concentrations.

The authors believe that the high rural ozone levels are primarily due to the transport of pollutants from a number of closely located urban sources, which cannot always be clearly identified.

(25) Stratospheric-Tropospheric Exchange Processes (Reiter, 1975a)

Qualitative descriptions and quantitative estimates are presented of various transport processes between stratosphere and troposphere. The seasonal changes of tropopause heights account for a flux of about 10 percent of the mass of the stratosphere in one hemisphere during the course of 1 year. This flux is balanced approximately by the seasonal shift of stratospheric air masses between the northern and southern hemispheres. Vertical transport through the Hadley cell transfers approximately 38 percent of the mass equivalent to one hemispheric stratosphere through the tropopause per year. This appears to be the most effective of all transport mechanisms. Large-scale eddies of the scale of cyclones and anticyclones transfer about 20 percent of stratospheric air through the tropopause per year. Small-scale and mesoscale diffusion processes at tropopause level probably account for the transfer of only 1 percent of stratospheric air. These mass flux estimates are in reasonable agreement with observed residence times of stratospheric pollutants.

(26) High Ozone Concentrations in Nonurban Atmospheres (Ripperton et al., 1974)

In the summer of 1973, ozone concentrations were measured at several rural locations in West Virginia, Pennsylvania, and Ohio. Chemiluminescent techniques were used and calibrations were performed using the standard method (neutral buffered KI). A C-45 aircraft was used to make O_3 measurements aloft, between and over the fixed field stations. Mean wind data at 900 mb from NOAA were used for trajectory analysis. Some of the results from the field program are as follows (see Figure 6 for station locations):

<u>Station Location</u>	<u>No. of Hours of Data</u>	<u>Percentage of Hours Exceeding O_3 Standard</u>	<u>Highest One-Hour O_3 Concentration (ppm)</u>
McHenry, Md.	1652	37	0.16
Kane, Pa.	2131	30	0.14
Coshocton, Ohio	1785	20	0.17
Lewisburgh, W.V.	1663	15	0.13

The aircraft data, some of which show lower concentrations aloft than at ground level, are used to exclude the possibility of significant stratospheric air intrusions. Collection of air samples in outdoor smog chambers indicates that local air is sufficiently contaminated to permit significant local ozone synthesis. It is contended that ozone in nonurban areas is not due to any given urban source but is a result of area-wide mixing. The interdispersed urban sources add to an air mix that already has natural as well as anthropogenic precursors, thereby making it impossible to identify precursor sources by trajectory analysis. The authors agree with the now well-accepted notion that ozone can be generated in a "spent photochemical system." They conclude that rural ozone is of surface origin.

(27) Investigation of Rural Oxidant Levels as Related to Urban Hydrocarbon Control Strategies (RTI, 1975)

A network of ground stations was established to document the occurrence of high ozone values in the rural areas of the eastern United States and their interrelationships with urban contaminants. A total of 11 stations (6 urban and 5 rural) were operational during the study period of 14 June to 31 August, 1974. Aircraft measurements were taken to obtain vertical ozone profiles and to determine the extent of urban plumes. In addition to meteorological parameters, THC, CH₄, O₃, NO₂, and selected hydrocarbons were measured.

It was found that the NAAQS for photochemical oxidants was exceeded twice as frequently at rural as at urban stations. Area-wide contamination of air masses was observed. It was not possible to track an urban plume for more than 30-50 miles downwind of Columbus, Ohio. High ozone concentrations were observed when a synoptic high pressure system moved over a given station, and high ozone levels persisted as long as the high pressure system remained in the vicinity.

Although no specific air trajectory terminating at the nonurban stations could be consistently associated with either high or low ozone concentrations, the results of the field measurement program still provide support for transport of ozone precursors from urban areas to rural stations under appropriate meteorological conditions. These results also imply that the control of hydrocarbon in any individual city will not necessarily prevent the occurrence of high rural ozone concentrations in excess of the NAAQS at any given nonurban site. The implication is that the release of hydrocarbons and oxides of nitrogen from anthropogenic or biogenic sources, located in either an urban or rural area, all combine to generate appreciable quantities of ozone over wide areas.

(28) Rural and Urban Ozone Relationships in New York State (Stasiuk and Coffey, 1974)

Ozone data from a number of air monitoring stations in New York State were analyzed. The rural monitoring stations were set up in Delaware (Mt. Utsayantha--elevation 3200 ft) and in the Northern Adirondacks (White Face Mountain--elevation 4980 ft). The urban sites were at Welfare Island (New York City); Kingston, Renesslaer, and Glen Falls in the Hudson River Valley; Syracuse in mid-state; and Buffalo in western New York. All O_3 data were measured using gas phase chemiluminescent analyzers and the federal calibration method.

High O_3 concentrations, often in excess of the NAAQS, were measured both at urban and nonurban locations. Average daily O_3 concentrations in rural areas--typically 30 to 100 ppb--were found to correlate well with the daily maximum ozone concentrations in the urban locations. The authors state that because of the high correlation between O_3 levels at widely separated urban and rural sites a common source for O_3 is suggested. Additionally, rough calculations of atmospheric O_3 overburden within the mixing layer show that the flux of O_3 into New York state can be an order of magnitude greater than that which might be generated by complete photochemical reactions of hydrocarbons emissions from New York state. On the basis of these rough estimates the authors question the likely effectiveness of oxidant abatement strategies.

IV SUMMARY OF AVAILABLE SOURCES OF OXIDANT/OZONE DATA

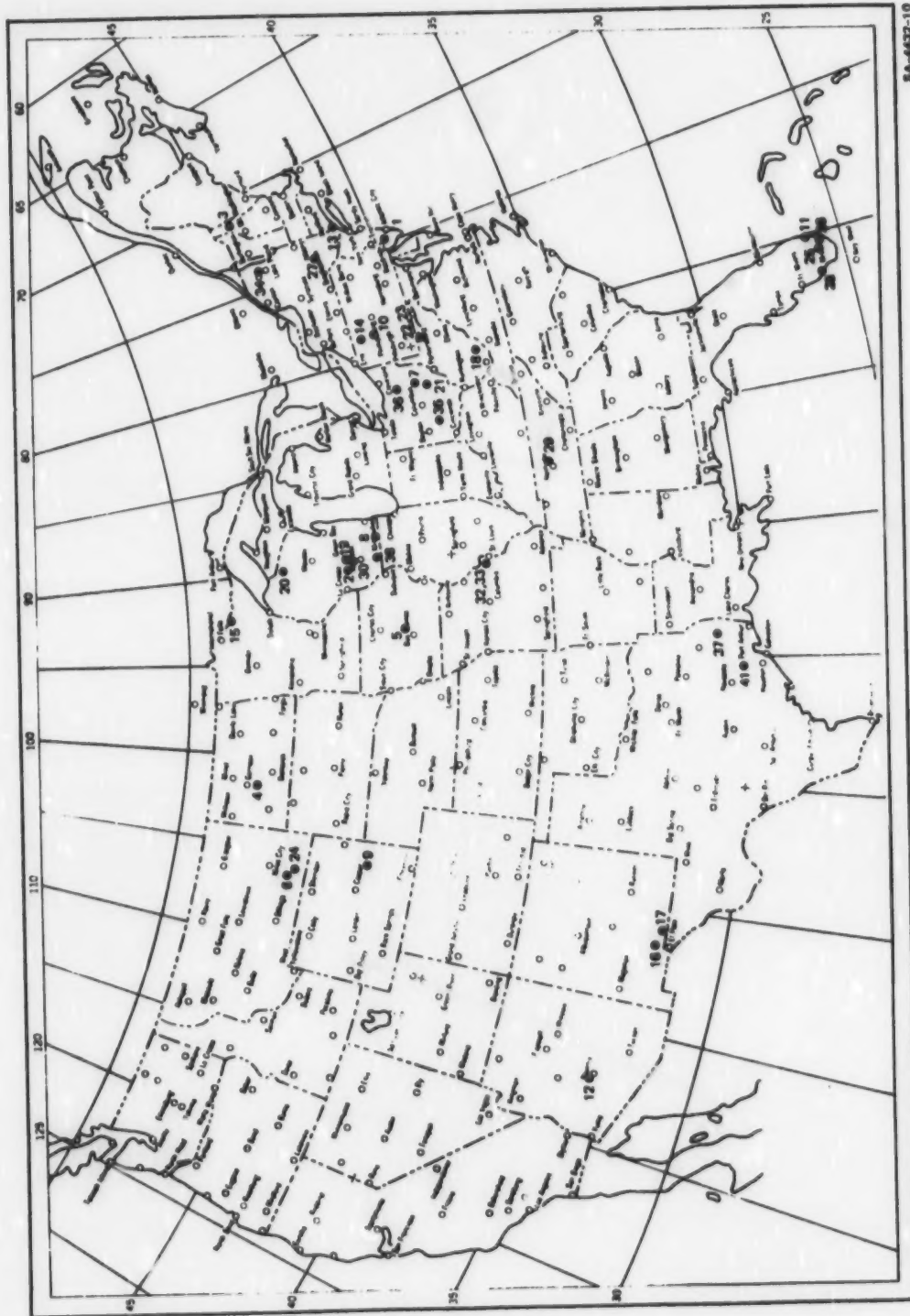
In this section descriptions are presented of sources of oxidant (or ozone) data believed to be suitable for studying the relation of oxidant levels to meteorological features. In searching for these data, we have carefully surveyed the EPA National Aerometric Data Bank (NADB), and have obtained information and data from various EPA central and regional offices, various state agencies, and a number of private organizations who have conducted or sponsored routine oxidant monitoring or special research studies.

Since the nonurban oxidant problem and its relation to meteorological processes is currently of considerable interest, we have excluded all urban and near-urban data. Hence this listing includes only those data that are believed to be relatively free from short-range urban contamination.

Particular efforts have been made to identify and include here sources of nonurban data in the eastern United States since this is a geographical region of much interest at the present time. Accordingly, data from the far western states have not been included in this compilation.

The two-year period 1973-1974 has been selected as optimum for the purposes of our later data analysis, and thus our review of the data has been restricted to this period. Any stations reporting less than 300 hours of data during this period have been excluded from this compilation.

The locations of the selected stations are shown in Figure 8. Following this, the data source descriptions are presented in alphabetical order by station name.



SA-4432-10

FIGURE 8 LOCATION OF SELECTED NONURBAN STATIONS (NUMBERS REFER TO DATA SOURCE DESCRIPTIONS INCLUDED IN THIS SECTION)

Data Source Number: 1

Station Name: Ancora (SAROAD Code 310740001F01)

Location: Camden County, New Jersey (39° 41' N. 74° 51' 45" W)

Responsible Organization: New Jersey Bureau of Air Pollution Control

Cognizant Individual/Organization: EPA Region II

Telephone: 212-264-2525

Type of Site: Rural-Agricultural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence

Period of Record Examined: 1973-1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, tape, or printout

Remarks: 3,368 observations reported during 1973-1974

Data Source Number: 2

Station Name: Badger (SAROAD Code 513160999F05)

Location: Sauk County, Wisconsin

Responsible Organization: Wis. Dept. of Nat. Resources, Air Pollution Control Section

Cognizant Individual/Organization: EPA Region V

Telephone: 302-353-5250

Type of Site: Rural - Agricultural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence

Period of Record Examined: 1973-1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, tape, or printout

Remarks: 827 observations reported during 1973-1974.

Data Source Number: 3

Station Name: Berlin (SAROAD Code 300040007F01)

Location: Coos County, New Hampshire (44° 27' N, 71° 11' 05" W)

Responsible Organization: New Hampshire Air Poll. Control Agency

Cognizant Individual/Organization: New Hampshire Air Poll. Control Agency

Telephone: _____

Type of Site: Suburban - industrial

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence

Period of Record Examined: 1973-1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, tape, or printout

Remarks: 4,547 observations reported during this period.

Data Source Number: 4

Station Name: Beulah

Location: 7 miles north of Beulah, North Dakota (47° 22' N, 101° 49' W)

Responsible Organization: American Natural Gas Service Company, Detroit, Michigan

Cognizant Individual/Organization: Albert Browning

Telephone: 313-965-1616

Type of Site: Rural-nonurban

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (Bendix 8002)

(Bendix Model 8002 Ozone Monitor)

Period of Record Examined: 15 June - 31 July 1974

Frequency of Observations: Hourly

Physical Form of Data Record: Printout

Remarks: Approximately 23% of all 1-hour average concentrations exceeded 0.08 ppm.

Values as high as 0.12 ppm were measured. The ozone values could not be attributed
to transport from urban sources. Lack of foliage, which would otherwise destroy
O₃, was postulated as one reason for the high O₃ values.

Data Source Number: 5

Station Name: Bondurant (SAROAD Code 163120024G02)

Location: Polk County, Iowa (41° 41' 59" N, 93° 28' 00" W)

Responsible Organization: Des Moines-Polk Co. Health Dept.

Cognizant Individual/Organization: EPA Region VII

Telephone: 816-374-5493

Type of Site: Rural - Agricultural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence

Period of Record Examined: 1973-1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, tape, or printout

Remarks: 2,324 observations reported during 1973-1974.

Data Source Number: 6
Station Name: Colstrip
Location: Rosebud County, Montana (45° 55'N, 106° 38' W)
Responsible Organization: Department of Natural Resources & Conservations,
Helena, Montana
Cognizant Individual/Organization: James Gelhaus

Telephone: 406-449-3454

Type of Site: Remote

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence

Period of Record Examined: December 1973 - May 1975

Frequency of Observations: Hourly

Physical Form of Data Record: Printout

Remarks: Data are missing for August and September 1974. Excellent remote location
with very low O₃ values (< 0.06 ppm) and a virtual absence of diurnal variations.
At no time did the O₃ level exceed 0.08 ppm, although a number of observations
were above 0.06 ppm.

Data Source Number: 7

Station Name: Coschocton

Location: Coschocton, Ohio (40° 15' N, 81° 54' W)

Responsible Organization: Research Triangle Institute

Cognizant Individual/Organization: J.J. Bufalini (EPA/ESRL)

Telephone: 919-549-8411

Type of Site: Rural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (Bendix #8002)

Period of Record Examined: 26 June - 30 September 1973

Frequency of Observations: Hourly

Physical Form of Data Record: Printout

Remarks: High O₃ concentrations were recorded. Limited O₃ data aloft were
also obtained.

Data Source Number: 8

Station Name: Darien (SARQAD Code 513680099F05)

Location: Walworth County, Wisconsin (42° 38' N, 88° 40' W)

Responsible Organization: Wisconsin Department of Natural Resources

Cognizant Individual/Organization: Ronald W. Becker

Telephone: 608-266-7588

Type of Site: Rural - Agricultural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (REM) and/or ultraviolet

Period of Record Examined: June-September 1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, tape, or printout

Remarks: 1,545 observations reported during this period. Monitoring in this
area is continuing in 1975.

Data Source Number: 9

Station Name: Douglas

Location: Converse County, near Douglas, Wyoming (42° 55' N, 105° 18' W)

Responsible Organization: Panhandle Eastern Pipeline Company

Cognizant Individual/Organization: Kenneth L. Ancell

Telephone: _____

Type of Site: Rural-remote

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (Bendix 8002)

Period of Record Examined: January - June 1974

Frequency of Observations: Hourly

Physical Form of Data Record: Printout

Remarks: All O₃ data recorded during this period were generally below 0.06 ppm.
A maximum of 0.076 ppm was measured on 21 June 1974

Data Source Number: 10

Station Name: DuBois

Location: DuBois, Pennsylvania (41° 10' N. 78° 44' W)

Responsible Organization: Research Triangle Institute

Cognizant Individual/Organization: J.J. Bufalini (EPA/ESRL)

Telephone: 919-549-8411

Type of Site: Rural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (Bendix 8002)

Period of Record Examined: 14 June - 31 August 1974

Frequency of Observations: Hourly

Physical Form of Data Record: Printout

Remarks: In addition to O₃, other species such as hydrocarbons, NO_x, etc., were
measured. Some aircraft data on vertical O₃ distributions were also obtained.

Data Source Number: 11

Station Name: Ft. Lauderdale (SARGAD Code 101260100G03)

Location: Ft. Lauderdale, Florida (26° 07'N, 80° 09' W)

Responsible Organization: EPA Region IV

Cognizant Individual/Organization: Louis Nagler

Telephone: 305-621-0561

Type of Site: Nonurban

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (Bendix 8002)

Period of Record Examined: January - June 1973

Frequency of Observations: Hourly

Physical Form of Data Record: Printout

Remarks: _____

Data Source Number: 12

Station Name: Glendale (SAROAD Code 030320001Q01)

Location: Glendale, Arizona (33° 33' 45", 112° 11' 15" W)

Responsible Organization: Maricopa County Health Dept.

Cognizant Individual/Organization: EPA Region IX

Telephone: 415-556-2320

Type of Site: Rural - near urban

Type of Pollutant Measured: O₃

Measurement Technique: Dasibi Ultraviolet

Period of Record Examined: 1973-1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, Tape, or Printout

Remarks: 1,808 observations reported during 1973-1974

Data Source Number: 13

Station Name: Greenwich (SAROAD Code 070330004F01)

Location: Greenwich, Connecticut (41° 4' 37" N, 73° 41' 56" W)

Responsible Organization: Conn. Dept. Envir. Protection

Cognizant Individual/Organization: EPA Region I

Telephone: 617-223-7210

Type of Site: Remote

Type of Pollutant Measured: 03

Measurement Technique: Chemiluminescence

Period of Record Examined: 1973-1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, tape, or printout

Remarks: 5315 observations reported during 1973-1974

Data Source Number: 14

Station Name: Kane

Location: Kane, Pennsylvania (41° 40' N, 78° 47' W)

Responsible Organization: Research Triangle Institute

Cognizant Individual/Organization: J.J. Bufalini (EPA/ESRL)

Telephone: 919-549-8411

Type of Site: Rural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (Bendix #8002)

Period of Record Examined: 26 June - 30 October 1973

Frequency of Observations: Hourly

Physical Form of Data Record: Printout

Remarks: High O₃ concentrations were recorded. Limited O₃ data aloft were
also obtained.

Data Source Number: 15

Station Name: Lake Kabetogama

Location: Lake Kabetogama, Minnesota (48° 27' N, 93° 02' W)

Responsible Organization: ---

Cognizant Individual/Organization: Ned Meyers (EPA/OAQPS)

Telephone: 919-688-8146

Type of Site: Rural-Near Urban

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (MEC 1100)

Period of Record Examined: 18 July - 21 August 1974

Frequency of Observations: Hourly

Physical Form of Data Record: Printout

Remarks: The measurements yielded low ozone values, with an hourly maximum
of 0.055 ppm.

Data Source Number: 16

Station Name: Las Cruces (SAROAD Code 320340010F01)

Location: Dona Ana County, New Mexico (32° 20' 20" N, 106° 49' 00" W)

Responsible Organization: State of New Mexico Envir. Improvement Agency

Cognizant Individual/Organization: EPA Region VI

Telephone: 214-749-1962

Type of Site: Rural-agricultural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence

Period of Record Examined: 1973-1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, tape, or printout

Remarks: 3,755 observations reported during 1973-1974

Data Source Number: 17

Station Name: La Union (SAROAD Code 320340008F02)

Location: Dona Ana County, New Mexico (31° 55' 50" N, 106° 37' 50" W)

Responsible Organization: State of New Mexico Envir. Improvement Agency

Cognizant Individual/Organization: EPA Region VI

Telephone: 214-749-1962

Type of Site: Rural-agricultural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence

Period of Record Examined: 1973-1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, tape, or printout

Remarks: 7,616 observations reported during 1973-1974

Data Source Number: 18

Station Name: Lewisburg

Location: Lewisburg, West Virginia (37° 50' N. 80° 22' W)

Responsible Organization: Research Triangle Institute

Cognizant Individual/Organization: J.J. Bufalini (EPA/ESRL)

Telephone: 919-549-8411

Type of Site: Rural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (Bendix #8002)

Period of Record Examined: 26 June - 30 September 1973

Frequency of Observations: Hourly

Physical Form of Data Record: Printout

Remarks: High near-ground O₃ concentrations were recorded. Limited O₃
data aloft were also obtained.

Data Source Number: 19

Station Name: MacKenzie Environmental Center (SAROAD Code 510600001F03)

Location: Columbia County, Wisconsin

Responsible Organization: Wisconsin Department of Natural Resources, Air Pollution Control Section

Cognizant Individual/Organization: EPA Region V

Telephone: 302-353-5250

Type of Site: Rural-industrial

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence

Period of Record Examined: 1973-1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, tape, or printout

Remarks: 12,665 observations reported during 1973-1974

Data Source Number: 20

Station Name: Manitowish Waters

Location: Vilas County, Wisconsin (46° N, 89° 54' W)
(6 miles south of Manitowish Waters on County K)

Responsible Organization: Wisconsin Dept. of Natural Resources

Cognizant Individual/Organization: Ronald W. Becker

Telephone: 608-266-7588

Type of Site: Rural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (REM) and/or Dasibi Ultraviolet

Period of Record Examined: June - September 1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, tape, or printout

Remarks: Monitoring in this area is continuing in 1975.

Data Source Number: 21

Station Name: McConnelsville

Location: McConnelsville, Ohio (39° 57' N, 82° 02' W)

Responsible Organization: Research Triangle Institute

Cognizant Individual/Organization: J.J. Bufalini (EPA/ESRL)

Telephone: 919-549-8411

Type of Site: Rural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (Bendix 8002)

Period of Record Examined: 14 June - 31 August 1974

Frequency of Observations: Hourly

Physical Form of Data Record: Printout

Remarks: In addition to O₃, other species such as hydrocarbons, NO_x, etc.
were also measured. Some aircraft data on vertical O₃ distributions were
also obtained.

Data Source Number: 22

Station Name: McHenry

Location: McHenry, Maryland (39° 36' N, 79° 16' W)

Responsible Organization: Research Triangle Institute

Cognizant Individual/Organization: J. J. Bufaline (EPA/ESRL)

Telephone: 919-549-8411

Type of Site: Rural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (Bendix 8002)

Period of Record Examined: 26 June - 30 September 1973

Frequency of Observations: Hourly

Physical Form of Data Record: Printout

Remarks: High near-ground O₃ concentrations were recorded. Limited O₃
data aloft were also obtained.

Data Source Number: 23

Station Name: McHenry

Location: McHenry, Maryland (39° 36' N, 79° 16' W)

Responsible Organization: Research Triangle Institute

Cognizant Individual/Organization: J.J. Bufalini (EPA/ESRL)

Telephone: 919-549-8411

Type of Site: Rural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (Bendix 8002)

Period of Record Examined: 14 June - 31 August 1974

Frequency of Observations: Hourly

Physical Form of Data Record: Printout

Remarks: In addition to O₃, other species such as hydrocarbons, NO_x, etc. were measured. Some aircraft data on vertical O₃ distributions were also obtained.

Data Source Number: 24

Station Name: McRae (SAROAD Code 271360028F03)

Location: Rosebud County, Montana (45° 45' 47" N, 106° 23' 09" W)

Responsible Organization: Montana State Air Quality Bureau

Cognizant Individual/Organization: EPA Region VIII

Telephone: 303-837-3895

Type of Site: Rural - Agricultural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence

Period of Record Examined: 1973-1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, tape, or printout

Remarks: 3570 observations reported during 1973-1974.

Data Source Number: 25

Station Name: Miami Jetport (SAROAD Code 100860008F02)

Location: Dade County, Florida (25° 51' 50" N, 80° 52' 10" W)

Responsible Organization: EPA Region IV

Cognizant Individual/Organization: EPA Region IV

Telephone: 404-526-5727

Type of Site: Remote

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence

Period of Record Examined: 1973-1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, tape, or printout

Remarks: 4,187 observations reported during 1973-1974.

Data Source Number: 26

Station Name: Miami West (SAROAD Code 10270009P05)

Location: Miami, Florida (25° 50' 06" N. 80° 14' 09" W)
(AT&T transmission station Hwy. 27 east of Tamiami Trail)

Responsible Organization: EPA Region IV

Cognizant Individual/Organization: Louis Nagler/EPA Region IV

Telephone: 305-621-0561

Type of Site: Rural - Near Urban

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (Eandix 8002)

Period of Record Examined: 1973-1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, tape, or ptintout

Remarks: 3,176 Observations reported during 1973-1974.

Data Source Number: 27

Station Name: Mt. Utsayantha

Location: Mt. Utsayantha, New York (74° 37' W, 42° 24' N)

Responsible Organization: N.Y. State Dept. of Env. Conservation

Cognizant Individual/Organization: William N. Stasiuk

Telephone: 518-457-5276

Type of Site: Remote

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence

Period of Record Examined: 1 August - 17 August 1973

Frequency of Observations: Hourly

Physical Form of Data Record: Printout

Remarks: High altitude location (3200 ft MSL)

Data Source Number: 28

Station Name: Naples (SAROAD Code 102880001F05)

Location: Naples, Florida (26° 01' 31"W, 81° 43' 50" W) (on Rookery Bay)

Responsible Organization: EPA Region IV

Cognizant Individual/Organization: Louis Nagler

Telephone: 305-621-0561

Type of Site: Rural - Near Urban

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (Bendix 8002)

Period of Record Examined: 1973-1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, tape, or printout

Remarks: 3342 observations reported during 1973-1974.

Data Source Number: 29

Station Name: Old Hickory (SAROAD Code 443320007F01)

Location: Sumner County, Tennessee (36° 17' 53" N, 86° 39' 11"W)
(10 miles northeast of Nashville)

Responsible Organization: Tenn. Dept. of Public Health, Div. of Air Pollution Control

Cognizant Individual/Organization: EPA Region IV

Telephone: 404-526-5727

Type of Site: Rural-Industrial

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence

Period of Record Examined: 1973-1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, tape, or printout

Remarks: 13,104 observations reported during 1973-1974.

Data Source Number: 30

Station Name: Poynette

Location: Columbia County, Wisconsin (43° 24' N, 89° 28' W)

Responsible Organization: Wisconsin Dept. of Natural Resources

Cognizant Individual/Organization: Ronald W. Becker

Telephone: 608-266-7588

Type of Site: Rural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (REM) and/or Dasibi Ultraviolet

Period of Record Examined: June - September 1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, tape, or printout

Remarks: Monitoring in this area is continuing in 1975.

Data Source Number: 31

Station Name: Prairie View

Location: Prairie View, Texas (30° 18' N, 95° 26' W)

Responsible Organization: Texas Air Quality Control Board

Cognizant Individual/Organization: Duane J. Johnson

Telephone: 512-451-5711

Type of Site: Suburban - Rural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminexcence (MEC #1100)

Period of Record Examined: 1 May - 1 September 1974

Frequency of Observations: Hourly

Physical Form of Data Record: Printout

Remarks: This site is located 40 miles north of Houston, Texas. Transport

from Houston was believed responsible for the high ozone values observed

at Prairie View. These measurements were part of the Goobar III Study.

Data Source Number: 32

Station Name: Queeny (Oxidant) (SAROAD Code 264300006G01)

Location: St. Louis County, Missouri (38° 59' 58" N, 91° 45' 46" W)

Responsible Organization: St. Louis Co. Health Dept., Air Pollution Control Div.

Cognizant Individual/Organization: EPA Region VII

Telephone: 816-374-5493

Type of Site: Rural - Near Urban

Type of Pollutant Measured: O_x

Measurement Technique: Neutral KI

Period of Record Examined: 1973-1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, tape, or printout

Remarks: 14,683 observations reported during 1973-1974.

Data Source Number: 33

Station Name: Queeny (Ozone) (SAROAD Code 264300006G01)

Location: St. Louis County, Missouri (38° 59' 58" N. 91° 45' 46" W)

Responsible Organization: St. Louis Co. Health Dept. APCD

Cognizant Individual/Organization: EPA Region VII

Telephone: 816-374-5493

Type of Site: Rural - Near Urban

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence

Period of Record Examined: 1973-1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, tape, or printout

Remarks: 1,823 observations reported during 1973-1974.

Data Source Number: 34

Station Name: White Face Mountain

Location: White Face Mountain, New York (44° 20' N, 74° 05' W)

Responsible Organization: N.Y. State Dept. of Env. Conservation

Cognizant Individual/Organization: William N. Stasiuk

Telephone: 518-457-5276

Type of Site: Remote

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence

Period of Record Examined: 1 August - 17 August 1973

Frequency of Observations: Hourly

Physical Form of Data Record: Printout

Remarks: Additional data have been obtained and will be made available shortly.
This is a high altitude location (4980 ft MSL).

Data Source Number: 35

Station Name: Wilmington

Location: Wilmington Industrial Air Park, Ohio (39° 20' N, 83° 48' W)

Responsible Organization: Research Triangle Institute

Cognizant Individual/Organization: J. J. Bufalini (EPA/ESRL)

Telephone: 919-549-8411

Type of Site: Rural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (Bendix 8002)

Period of Record Examined: 14 June - 31 August 1974

Frequency of Observations: Hourly

Physical Form of Data Record: Printout

Remarks: In addition to O₃, other species such as hydrocarbons, NO_x, etc.,
were measured. Some aircraft data on vertical O₃ distributions were also
obtained.

Data Source Number: 36

Station Name: Wooster

Location: Wooster, Ohio (40° 50' N, 81° 56' W)

Responsible Organization: Research Triangle Institute

Cognizant Individual/Organization: J. J. Bufalini (EPA/ESRL)

Telephone: 919-549-8411

Type of Site: Rural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (Bendix 8002)

Period of Record Examined: 14 June - 31 August 1974

Frequency of Observations: Hourly

Physical Form of Data Record: Printout

Remarks: In addition to O₃, other species such as hydrocarbons, NO_x, etc.,
were measured. Some aircraft data on vertical O₃ distributions were also
obtained.

Data Source Number: 37

Station Name: Yellow Pine

Location: Sabine National Forest, Texas (31° 20' N. 96° 00' W)

Responsible Organization: Texas Air Quality Control Board

Cognizant Individual/Organization: Duane J. Johnson

Telephone: 512-451-5711

Type of Site: Rural - Remote

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (MEC #1100)

Period of Record Examined: April - June 1974

Frequency of Observations: Hourly

Physical Form of Data Record: Printout

Remarks: This location is 85 miles north of Beaumont and 135 miles northeast
of Houston. O₃ values exceeded 0.08 ppm only twice during this period.
Transport from urban sources was not responsible for high O₃ values.
Local synthesis was predominant.

Data Source Number: 38

Station Name: Yellowstone Lake (SAROAD Code 511720001F05)

Location: Lafayette County, Wisconsin (42° 46' N, 89° 54' W)

Responsible Organization: Wisconsin Dept. of Natural Resources

Cognizant Individual/Organization: Ronald W. Becker

Telephone: 608-266-7588

Type of Site: Rural

Type of Pollutant Measured: O₃

Measurement Technique: Chemiluminescence (REM) and/or Dasibi Ultraviolet

Period of Record Examined: June - September 1974

Frequency of Observations: Hourly

Physical Form of Data Record: Cards, tapes, or printout

Remarks: 3,205 observations were reported during this period. Monitoring in
this area is continuing in 1975.

REFERENCES AND COMPREHENSIVE BIBLIOGRAPHY

- Aldaz, L., 1967: Surface air radioactivity and ozone at Admundsen-Scott station (90o). Antarctica, Nature, 215, 722-723.
- Aldaz, L., 1969: Flux measurements of atmospheric ozone over land and water. J. Geophys. Res., 74, 6943-6946.
- Alley, F. C., and L. A. Ripperton, 1961: The effect of temperature on photochemical oxidant production in a bench scale reaction system. J. Air Poll. Contr. Assoc., 11, 581-584.
- Altshuller, A. P., and J. J. Bufalini, 1965: Photochemical aspects of air pollution: A review. Photochem. and Photobiol., 4, 94-146.
- Altshuller, A. P., and J. J. Bufalini, 1971: Photochemical aspects of air pollution: A review. Env. Sci. and Tech., 5, 36-64.
- Altshuller, A. P., W. A. Lonneman, F. D. Sutterfield, and S. L. Kopezynski, 1971: Hydrocarbons composition of the atmosphere over the Los Angeles basin - 1967. Env. Sci. Tech., 5, 1009-1016.
- Altshuller, A. P., 1975: Evaluation of oxidant results at CAMP sites in the United States. J. Air Poll. Contr. Assoc., 25, 19-24.
- Attmannspacher, W., and R. Kartmannsgruber, 1973: On extremely high values of ozone near the ground, proceedings of the symposium on atmospheric ozone, Arosa, August 21-25, 1972. Pure and Appl. Geophys., 106-108, 1091-1095.
- Baboolal, L. B., I. H. Tomback, and M. I. Smith, 1975: Mesoscale flows and ozone levels in a rural California coastal valley. Presented at the First Conference on Regional and Mesoscale Modeling, Analysis, and Prediction of the American Meteorological Society, May 6-9, Las Vegas, Nevada.
- Bach, W. D., 1975: Investigation of ozone and ozone precursor concentrations at nonurban locations in the eastern United States. Phase II, Research Triangle Institute, prepared for Environmental Protection Agency, Research Triangle Park, N.C., EPA Report 450/3-74-034-a.
- Bach, W. D., and T. Hagedorn, 1971: Atmospheric pollution: its spatial distribution over an urban area. Proc. Assoc. Amer. Geogr., 3, 19-24.
- Becker, W. B., 1974: Ozone monitoring--Wisconsin, Summer, 1974. Interim Report to EPA from the Department of Natural Resources, State of Wisconsin.

- Becker, K. H., U. Schurath, and H. Seitz, 1974: Ozone-olefin reactions in the gas phase, rate constants and activation energies. Int. J. Chem. Kinetics, 6, 725-739.
- Bell, G. B., 1960: Meteorological conditions during oxidant episodes in coastal San Diego County in October and November, 1959. California State Department of Public Health, Berkeley, California.
- Blumenthal, D. L., A. R. MacLeod, T. B. Smith, G. R. Markowski, and T. M. Mills, 1973: Air quality and ventilation studies in the Valdez Basin-Winter 1973. MRI Final Report to Aleyska Pipeline Service Co., Houston, Texas, MRI 73 FR-1085.
- Blumenthal, D. L., J. A. Anderson, and G. J. Sem, 1974: Characterization of Denver's urban plume using an instrumented aircraft. Presented at meeting of the Air Pollution Control Association, Denver, June 9-13
- Blumenthal, D. L., et al., 1974: Three-Dimensional pollutant gradient study program--1972-1973, MRI Project 74FR-1262, Prepared for California Air Resources Board, MRI, Altadena, California.
- Blumenthal, D. L., et al., November 1974: Determination of the feasibility of the long-range transport of ozone or ozone precursors. Meteorology Research Inc., prepared for Environmental Protection Agency, Research Triangle Park, N.C., EPA Report 450/3-74-061.
- Breiland, J. G., 1968: Some large-scale features of the vertical distribution of atmospheric ozone associated with the thermal structure of the atmosphere. J. Geophys. Res., 73, 5021-5028.
- Breiland, J. R., 1964: Vertical distribution of atmospheric ozone and its relation to synoptic meteorological conditions. J. Geophys. Res., 69, (18), 3801-3808.
- Bruntz, S. M., W. S. Cleveland, T. E. Graedel, B. Kleiner, and J. L. Warner, 1974: Ozone concentrations in New Jersey and New York, 1974: Statistical association with related variables. Science, 186, 257-259.
- Bruntz, S. M., et al., 1974: The dependence of ambient ozone on solar radiation, wind, temperature, and mixing height, Symposium on Turbulent Diffusion and Air Pollution, Amer. Meteorol. Soc., 125-128.
- Bufalini, J. J., T. A. Walter, and M. M. Bufalini, 1976: Ozone formation potential of organic compounds. Env. Sci. and Tech., 10, 908-912.
- Calvert, J. G., 1976: Hydrocarbon involvement in photochemical smog formation in Los Angeles atmosphere. Env. Sci. and Tech., 10, 256-262.

- Calvert, J. G., 1976: Test of the theory of ozone generation in Los Angeles atmosphere. Env. Sci. and Tech., 10, 248-255.
- Cavanagh, L. A., and J. H. Smith, 1973: Atmospheric photochemical smog measurements over San Francisco Bay. SRI Final Report, Coordinating Research Council CAPA-12-72 and Environmental Protection Agency (EPA) Contract 68-02-1009, SRI Projects 2092 and 2098, Stanford Research Institute, Menlo Park, California.
- Chameides, W., and J.C.G. Walker, 1973: A photochemical theory of tropospheric ozone. J. Geophys. Res., 78, 8751-8760.
- Chameides, W. L., and D. H. Stedman, 1976: Ozone formation from NO_x in "clean air". Env. Sci. and Tech., 10, 150-154.
- Chameides, W. L., and D. H. Stedman, 1976: Tropospheric ozone: Coupling transport and photochemistry. Presented at The Non-urban Tropospheric Composition Symposium, Hollywood, Florida, November 10-12.
- Chang, T. Y., and B. Weinstock, 1976: Net ozone formation in rural atmospheres. Presented at the International Conference on Photochemical Oxidant Pollution and its Control, September 12-17, Raleigh, North Carolina.
- Chatfield, R. and H. Harrison, 1976: Tropospheric ozone I: evidence for higher background values, submitted to J. Geophys. Res.
- Ibid., 1976: Tropospheric ozone II: variations along a meridional band, submitted to J. Geophys. Res.
- Chatfield, R. and R. A. Rasmussen, 1976: An assessment of the continental lower tropospheric ozone budget. Presented at the International Conference on Photochemical Oxidant Pollution and Its Control, September 12-17, Raleigh, North Carolina.
- Cleveland, W. S., et. al., 1974: Sunday and workday variations in photochemical air pollutants in New Jersey and New York. Science, 186, 1037-1038.
- Cleveland, W. S., and B. Kleiner, 1975: Transport of photochemical air pollution from the Camden-Philadelphia urban complex. Env. Sci. and Tech., 99, 869-872.
- Cleveland, et al., 1975: The analysis of ground-level ozone data from New Jersey, New York, Connecticut and Massachusetts: data quality assessment and temporal and geographical properties (unpublished manuscript).
- Cleveland, W. S., B. Kleiner, J. E. McRae and J. L. Warner, 1976: Photochemical air pollution: transport from the New York City area into Connecticut and Massachusetts. Science, 191, 179-181.

- Coffey, P. E., and N. W. Stasiuk, 1975: Evidence of atmospheric transport of ozone into urban areas. Env. Sci. and Tech., 9, 59-63.
- Cole, A. F., and M. Katz, 1966: Summer ozone concentrations in southern Ontario in relation to photochemical aspects and vegetation damage, J. Air. Poll. Contr. Assoc., 16 (4), 201-206.
- Corn, M., et al., 1975: Photochemical oxidants: sources, sinks and strategies. J. Air Poll. Contr. Assoc., 25, 16-18.
- Cox, R. A., et al., 1975: Long-range transport of photochemical ozone in northwestern Europe. Nature, 255, 118-121.
- Crutzen, P. J., 1971: Ozone production rates in an oxygen-hydrogen-nitrogen oxide atmosphere. J. Geophys. Res., 76, 7311-7327.
- Crutzen, P. J., 1974: Photochemical reactions initiated by and influencing ozone in unpolluted tropospheric air. Tellus, 26, 47-57.
- Dabberdt, W. F. and H. Singh, 1977: Objective evaluation of emergency plans for oxidant control. J. of Air Poll. Contr. Assoc. (in press).
- Danielsen, E. F., 1960: A determination of the mass transported from stratosphere to troposphere over North America during a thirty-six hour interval, Mitt. Deut. Wett., 20, 10-11.
- Danielsen, E. F., 1961: Trajectories: isobaric, isentropic and actual. J. Meteorol., 18, 479-486.
- Danielsen, E. F., 1964: Report on project springfield. Report DASA-1517, Defense Atomic Support Agency, Washington, D.C.
- Danielsen, E. F. and V. A. Mohnen, 1976: Project dust storm report: Ozone measurements and meteorological analyses of tropopause folding. Proc. The Non-urban Tropospheric Composition Symposium, Hollywood, Florida, November 10-12, pp 17.1-17.13.
- Darnall, K. R., A. C. Lloyd, A. M. Winer and J. N. Pitts, Jr.: Reactivity scale for atmospheric hydrocarbons based on reaction with hydroxyl radical. Env. Sci. and Tech., 10, 692-697
- Demerjian, K. L., J. A. Kerr, and J. G. Calvert, 1974: The mechanism of photochemical smog formation. Advances in Environmental Science, Vol. 4, editors. J. N. Pitts, Jr. and R. L. Metcalf, New York: John Wiley, 262 pp.
- Demore, W. 1974: Comparison of oxidant calibration procedures, Final Report ARB-75-4-4, for the Air Resources Board, California.
- Dimitriades, B. and S. B. Joshi, 1976: Application of reactivity criteria in oxidant-related emission control in USA. Presented at the International Conference on Photochemical Oxidant Pollution and Its Control, September 12-17, Raleigh, North Carolina.

- Dimitriadis, B., 1977: Oxidant control strategies. Part I. Urban oxidant control strategy derived from existing smog chamber data. Env. Sci. and Tech., 11, 80-88.
- Dodge, M. C., 1976: Combined use of modeling techniques and smog chamber data to derive ozone-precursor relationships. Presented at the International Conference on Photochemical Oxidant Pollution and Its Control, September 12-17, Raleigh, North Carolina.
- Dutsch, H. U., January, 1966: Two years of regular ozone soundings over Boulder, Colorado. NCAR TN-10, National Center for Atmospheric Research, Boulder, Colorado, 443 pp.
- Dutsch, H. U., 1971: Photochemistry of atmospheric ozone, in Advances in Geophysics, vol. 15, pp. 219-322. New York: Academic Press.
- Dutsch, H. U., 1974: Ozone research, present and future, in Proc. Int. Conf. on Structure, Composition and General Circulation of the Upper and Lower Atmospheres and Possible Anthropogenic Perturbations, Vol. 1, pp. 321-339. Toronto, International Association Meteor. Atmos. Phys.
- Edinger, J. G., 1961: Changes in the depth of the marine layer over the Los Angeles Basin. J. Meteorol., 16, 219-226.
- Edinger, J. G., M. H. McCutchan, P. R. Miller, B. C. Ryan, M. J. Schroeder, and J. V. Behar, 1972: Penetration and duration of oxidant air pollution in the south coast air basin of California. J. Air Poll. Contr. Assoc., 22, 882-886.
- Edinger, J. G., 1973: Vertical distribution of photochemical smog in Los Angeles basin. Env. Sci. and Tech., 7, (3), 247-252.
- EPA, 1971: Mount Storm, West Virginia-Gorman, Maryland-Keyser, West Virginia air pollution abatement activity. Environmental Protection Agency, Research Triangle Park, N. C., EPA Publication APTD-0656.
- EPA, 1974: Investigation of ozone and ozone precursor concentrations at nonurban locations in the eastern United States, phase I. Environmental Protection Agency, Research Triangle Park, N.C., EPA Report 450/3-74-034.
- EPA, 1975: Control of photochemical oxidants--technical basis and implications of recent findings. Environmental Protection Agency, Research Triangle Park, N.C., EPA Report 450/2-75-005.

- Fabian, P., 1973: A theoretical investigation of tropospheric ozone and stratospheric-tropospheric exchange processes. Pure and Appl. Geophys., 104-108, 1044-1057.
- Fabian, P., and C. E. Junge 1970: Global rate of ozone destruction at the earth's surface. Arch. Meteorol. Geophys. Biokl. Ser. A, 19, 161-172.
- Fabian, P. and P. G. Pruchniewicz, 1976: Final Report on Project "Tropospherisches Ozon", Max-Planck-Institute für Aeronomie, Germany.
- Falconer, P. D. and J. D. Holdeman, 1976: Measurements of Atmospheric Ozone Made from a GASP-Equipped 747 Airliner: Mid-March, Vol. 3, pp 101-104.
- Farrow, L. A., T. E. Groedel and T. A. Weber, 1976: Urban kinetic chemistry under altered source conditions. Presented at the International Conference on Photochemical Oxidant Pollution and Its Control, September 12-17, Raleigh, North Carolina.
- Federal Register, 1971: National Primary and Secondary Ambient Air Quality Standards, Vol. 36 (Nos. 84, 158, and 228), pp. 8187; 15,491; 22,384.
- Fishman, J. and D. J. Crutzen, 1976: A numerical investigation of tropospheric photochemistry using a one-dimensional model. Proc. "The Non-Urban Tropospheric Composition Symposium", Hollywood, Florida, November 10-12, pp. 23.1-23.15.
- Fowler, et al., 1975: The Goober III study, Texas air control board, (unpublished manuscript).
- Fox, D.L., R.M. Kames, and H.E. Jeffries, 1975: Photochemical smog system: effect of dilution on ozone formation. Science, 188, 1113.
- Gay, B.W. and R. Arnts, 1976: The chemistry of naturally emitted hydrocarbons. Presented at the International Conference on Photochemical Oxidant Pollution and Its Control, September 12-17, Raleigh, North Carolina.
- Galbally, I. E., 1968: Ozone variation and destruction in the atmospheric surface layer. Nature, 218, 456-457.
- Galbally, I. E., 1971: Ozone profiles and ozone fluxes in the atmospheric surface layer. Quart J. Roy. Meteorol. Soc., 97, 18-29.
- Gloria, H. R., et al., 1974: Airborne survey of major air basins in California, J. Air Poll. Contr. Assoc., 24 (7), 645-652.

- Godson, W. L., 1960: The representation and analysis of vertical distributions of ozone. Quart. J. Roy. Meteorol. Soc., 88, 220.
- Godson, W. L., 1960: Total ozone and the middle stratosphere over arctic and subarctic areas in winter and spring. Quart. J. Roy. Meteorol. Soc., 86, 301.
- Gotz, F. W. P., A. R. Meeham, and G. M. B. Dobson, 1934: The vertical distribution of ozone in the atmosphere. Proc. Roy. Soc. London, A145, 416.
- Graedel, T. E., L. A. Farrow, and T. A. Weber, 1974: The effects of variations of in-bulk meteorological parameters on ozone concentrations-in Proc. Symposium on Turbulent Diffusion and Air Pollution. pp. 115-120. Amer. Meteorol. Soc.
- Haering, George W., 1977: Ozone sources of an urban area as indicated by altitude data (unpublished manuscript).
- Hawke, G. S., and D. Iverach, 1974: A study of high photochemical pollution days in Sydney, N.S.W. Atm. Env., 8, 597-608.
- Hecht, T.A., Seinfeld, J.H., and M.C. Dodge, 1974: Further development of generalized kinetic mechanism for photochemical survey. Env. Sci. and Tech. 8 (4), 327-339.
- Heffter, J. L. and A. D. Taylor, 1975: A regional-continental scale transport, diffusion and deposition model, Part I: Trajectory model. NOAA Tech. Memo ErL ARL-50, pp. 1-16.
- Hering, W. S., and T. R. Borden, Jr., 1964a: Ozonesonde observations over North America Vol. 1, Air Force Cambridge Research Laboratories, AFCRL-64-30(I).
- Hering, W. S., and T. R. Borden, Jr., 1964b: Ozonesonde observations over North America, Vol. 2, Air Force Cambridge Research Laboratories, AFCRL-64-30(II).
- Hering, W. S., and T. R. Borden, Jr. 1964b: Ozonesonde observations over North America, Vol. 3, Air Force Cambridge Research Laboratories, AFCRL-64-30(III).
- Hering, W.S., and T. R. Borden, Jr., 1967: Ozonesonde observations over North America, Vol. 4, Air Force Cambridge Research Laboratories, AFCRL-64-30(IV).
- Holzworth, G. C., 1969: Large-scale weather influences on community air pollution potential in the United States. J. Air. Poll. Contr. Assoc., 9 (4), 248-254.

- Holzworth, G.C., 1972: Mixing Heights, Wind Speeds, and Potential for Urban Air Pollution Throughout the Contiguous United States, EPA, Research Triangle Park, N.C., p. 118.
- Huie, R. E., and J. T. Herron, September 16, 1974: Temperature dependence of the rate constants for reactions of ozone with some olefins. Presented at Symposium on Chemical Kinetic Data for the Lower and Upper Atmosphere, Warrenton, VA.
- ICAFAR, 1975: 1974 Indianapolis Summer Ozone Study, Indianapolis Center for Advanced Research, Indianapolis, Indiana.
- Jacobson, J. S., and G. D. Salottolo, 1975: Photochemical oxidants in the New York-New Jersey metropolitan area. Atmos. Environ. 9, 321-332.
- Jeffries, H.E., J.E. Sickels, and L.A. Ripperton, 1974: Ozone transport phenomena: observed and simulated. Presented as Paper 76-14.3 at the 69th Annual APCA Meeting at Portland, Oregon, June 27-July 1.
- Johnson, W.B. and H.B. Singh, 1975: Oxidant layers aloft: their origin and significance. Presented at the International Conference on Photochemical Oxidant Pollution and Its Control, September 12-17, Raleigh, North Carolina.
- Johnston, D. R., 1973: Investigation of high ozone concentrations in the vicinity of Garrett County, Maryland and Preston County, West Virginia. Research Triangle Institute, prepared for Environmental Protection Agency, Research Triangle Park, N.C., EPA Report R4-73-019.
- Jones, D.C. and M. LaHue, 1976: Background ozone concentration in Western Colorado in Proc. Ozone/Oxidant Interactions with the Total Environment Speciality Conference, pp. 252-267. APCA Southwest Section, March 1976.
- Junge, C. E., 1962: Global ozone budget and exchange between stratosphere and troposphere. Tellus, 14, 363-377.
- Junge, C. E., 1963: Air Chemistry and Radioactivity in International Geophysics Survey, Vol. 4, pp. 49-58, New York, Academic Press.
- Junge, C. E., 1973: Studies of global exchange processes in the atmosphere by natural and artificial tracers. J. Geophys. Res. 68, (13), 3849-3856.
- Kaupert, E. K., 1960: The zone of discontinuity between the land and sea breezes and its importance to southern California air pollution studies. Bull. Amer. Meteor. Soc., 41, 410-422.
- Kelly, J. J. 1970: Atmospheric ozone investigation at Barrow, Alaska, During 1966-1967. Report 2, Department of Atmospheric Sciences, University of Washington, Sciences Report to Office of Naval Research, NR 307-252.

- Kelly, J. J., 1973: Surface ozone in the arctic atmosphere, Pure and Appl. Geophys., 106-108, 1107-1115.
- Kinosian, J. R., and S. Duckworth, 1973: Oxidant trends in the south coast air basin. California Air Resources Board Report.
- Kisten, S.L. and R.V. Carter, 1976: Ozone measurements in the rural southern United States. Presented at the 69th Annual JAPCA Meeting at Portland, Oregon.
- Knox, J. R., and R. Lange, 1974: Surface air pollutant concentration frequency distributions: implications for urban modeling. J. Air. Poll. Contr. Assoc. 24, (1), 48-53.
- Kopczynski, S. L., W. A. Lonneman, T. Winfield, and R. Seila, 1975: Gaseous pollutants in St. Louis and other cities. J. Air. Poll. Contr. Assoc., 25, (3), 251-255.
- Komhyr, W. D., and P. R. Stickse, 1967: Ozonosonde observations 1965-1966, Vol. 1, U.S. Department of Commerce, Environmental Science Services Administration, Boulder, Colorado, ESSA Technical Report IER 51-IASI.
- Krey, P. W., M. Schonberg, and L. Toonkel, 1974: Updating Stratospheric Inventories to January 1973, Report HASL-281, U.S. Atomic Energy Communications, New York, pp. 1/30-1/42.
- Kroening, J. L., and E. P. Ney, 1962: Atmospheric ozone. J. Geophys. Res., 67, 1881.
- Lamb, R., 1976: A case study of stratospheric ozone affecting ground-level oxidant concentrations (unpublished manuscript).
- Lawrence, E. N., 1971: Urban climate and day of the week. Atmos. Env., 5, 935-938.
- Lea, D. A., 1968: Vertical ozone distribution in the lower troposphere near an urban pollution complex. J. Appl. Meteorol. 7, 252-267.
- Leighton, P. A., 1961: Photochemistry of Air Pollution. New York, Academic Press.
- Leone, I. A., E. Brennan, and R. H. Daines, 1962: Daily fluctuation of phytotoxic air pollutants in three New Jersey communities as influenced by certain meteorological parameters. Plant Dis. Repr. 46, 140-144.
- Leone, I. A., E. Brennan, and R. H. Daines, 1968: The relationship of wind parameters in determining oxidant concentrations in two New Jersey communities. Atmos. Env., 2, 25-33.

- Levy, H. H., 1974: Photochemistry of the troposphere. Advances in Photochemistry, pp. 370-524.
- Lillian, D., 1972: Formation and destruction of ozone in a simulated natural system (nitrogen dioxide and α -Pinene + hv) in Photochemical Smog and Ozone Reactions. American Chemical Society.
- List, R. J., and K. Telegadas, 1969: Using radioactive tracers to develop a model of the circulation of the stratosphere. J. Atmos. Sci., 26, (5), 1128-1136.
- Lodge, J. P. and J. B. Pate, 1963: Atmospheric gases and particulates in Panama, Science, 153, 408-410.
- London, J. and J. Kelly, 1974: Global trends in total atmospheric ozone. Science, 184, 987-989.
- Lonneman, W.A., 1976: Ozone and Hydrocarbon Measurements in Recent Oxidant Transport Studies. Presented at the International Conference on Photochemical Oxidant Pollution and Its Control, September 12-17, Raleigh, North Carolina.
- Lonneman, W.A., J.J. Bufalini, and R.L. Seila, 1976: PAN and oxidant measurements in ambient atmospheres. Env. Sci. and Tech., 10, 374-380.
- Loville, J. E., and A. Miller, 1968: The vertical distribution of ozone over the San Francisco Bay Area. J. Geophys. Res., 73, 5073-507.
- Loville, J. E., 1972: The global distribution of total ozone as determined by the NIMBUS III satellite infrared interferometer-spectrometer. Colorado State University, Ph.D. Dissertation, 72 pp.
- Ludwick, J.D., T.D. Fox and L.L. Wendell, 1976: Ozone and radionuclide correlations in air of marine trajectory at Quillayute, Washington. J. of Air Poll. Contr. Assoc., 26, 565-569.
- Ludwig, F. L., and J. H. S. Kealoha, 1974: Present and prospective San Francisco Bay Area air quality. Prepared for Wallace, McHarg, Roberts, and Todd, and the Metropolitan Transportation Commission, SRI Project 3274, Stanford Research Institute, Menlo Park, California.
- Ludwig, F.L., et al, 1977: The relation of oxidant levels to precursor emissions and meteorological features. Final Report, EPA Contract 68-02-2084, SRI Project 4432, Stanford Research Institute, Menlo Park, California.
- Ludwig, F.L., W.B. Johnson, R.E. Ruff, and H.B. Singh, 1976: Important factors affecting rural ozone concentration. Presented at the International Conference on Photochemical Oxidant Pollution and Its Control, September 12-17, Raleigh, North Carolina.

- Ludwig, F.L. and E. Shelar, 1977: Ozone in the northeastern United States. Final Report, EPA (Region 1) Contract 68-02-2352, SRI Project 4967, Stanford Research Institute, Menlo Park, California.
- Lund, I., 1963: Map pattern classifications by statistical methods. J. Appl. Meteorol., 2, 56-65.
- Lusis, M.A., et al., 1976: Aircraft O₃ measurements in the vicinity of Toronto, Canada. Presented as Paper 76-7.1 at the 69th Annual APCA Meeting at Portland, Oregon, June 27-July 1.
- Lyons, W.A. and H.S. Cole, 1976: Photochemical oxidant transport: mesoscale lake breeze and synoptic-scale aspects. J. of App. Met. 15, 733-743.
- Machta, L., K. Telegadas, and R. J. List, 1970: The slope of surfaces of maximum tracer concentration in the lower stratosphere. J. Geophys. Res., 75, (12), 2279-2289.
- Mackee, M. C., 1961: Atmospheric ozone in northern Greenland. J. Air Poll. Contr. Assoc., 11, 562-565.
- Mahlman, J. D., 1964: Relation of stratospheric-tropospheric mass exchange mechanisms to surface radioactivity peaks. Arch. Meteorol. Geophys. Biok. Ser. A., 15, 1-25.
- Martinez, E. L., 1975: Temporal-spatial variations of nonurban ozone concentrations and related meteorological factors. Environmental Protection Agency, Research Triangle Park, N.C. (unpublished manuscript).
- Mendonca, B. G., 1969: Local wind circulation on the slopes of Mauna Loa. J. Appl. Met., 8, 533-541.
- Miller, A., 1974: Rural and urban ozone relationships (letter to the editor). J. Air Poll. Contr. Assoc., 24, 819.
- Miller, A., and D. Ahrens, 1970: Ozone within and below the west coast temperature inversion. Tellus, 22, (3), 328.
- Miller, P. R., M. H. McCutchan, and H. P. Milligan, 1972: Oxidant air Pollution in the central valley, Sierra Nevada foothills, and Mineral King Valley of California, Atm. Env., 6, 623.
- Meyer, E. L., 1977: Establishing organic emission control strategies as a function of geographic location. EPA Draft Internal Memorandum.
- Mohnen, V.A., A. Hogan, R. Whitby, and P. Coffey, 1976: Ozone measurements in rural areas. Proc. The Non-Urban Tropospheric Composition Symposium, Hollywood, Florida, Nov. 10-12, pp. 20.1-20.8.

- Mosher, J. C., W. G. MacBeth, M. J. Leonard, T. P. Mullins, and M. F. Brunelle, 1970: The distribution of contaminants in the Los Angeles basin resulting from atmospheric reactions and transport. J. Air Poll. Contr. Assoc., 20, 35-42.
- Munn, R. E., and B. Bolin, 1971: Review paper--global air pollution--meteorological aspects. Atm. Env., 5, 363-402.
- NAS, 1976: Vapor-phase organic pollutants-volatile hydrocarbons and oxidation products. National Research Council, Washington, D.C.
- NAS, 1974: Air quality and automobile emission control (prepared for the Committee of Public Works, United States Senate). National Academy of Sciences, 3, 1-137.
- Neiburger, M. N., N. A. Renzetti, L. H. Rogers, and R. Tice, 1955: An aerometric survey of the Los Angeles basin, August-November, 1954--interpretation of results. Air Pollution Foundation Report, 9, N. A. Renzetti, ed. pp. 116-200.
- Niebor, H. and J. Van Ham, 1976: Peroxyacetyl nitrate (PAN) in relation to ozone and some meteorological parameters at Delft in the Netherlands. Atm. Env., 10, 115-120.
- Newell, R. E., 1964: The circulation of the upper atmosphere. Sci. Amer., 210, (3), 62-74.
- Newell, R. E., H. W. Brandli, and D. A. Widen, 1966: Concentration of ozone in surface air over Greater Boston in 1965. J. Appl. Meteorol., 5, (5), 740-741.
- Normand, C., 1951: Some recent work on ozone. Quart. J. Roy. Meteor. Soc., 77, 474.
- Noxon, J.F., 1975: NO₂ in the stratosphere and troposphere by ground-based absorption spectroscopy, Science, 189, 547-549.
- Oltmans, S.J. and W. Komhyr, 1976: Surface ozone in Antarctica, J. of Geophys. Res., 81, 5359-5364.
- Paskind, J., and J. R. Kinosian, 1974: Hydrocarbon, oxides of nitrogen, and oxidant pollution relationships in the atmosphere over California cities. Paper presented at 67th Annual Meeting, Air Pollution Control Association, Denver, Colorado.
- Pitts, J.N., et al, 1976: Corrected south coast air basin oxidant data: some conclusions and implications. Env. Sci. and Tech., 10, 794-801.
- Polgar, L.G., and R.J. Londergan, 1976: Surface and airborne ozone and precursor concentrations from a medium sized city. Presented as Paper 76-14.2 at the 69th Annual APCA Meeting at Portland, Oregon, June 27-July 1.

- Pruchniewicz, P. G., 1973: The average tropospheric ozone content and its variation with season and latitude as a result of the global ozone circulation. Pure and Appl. Geophys., 106-108, 1058-1073.
- RTI, 1975: Investigation of rural levels as related to urban hydrocarbon control strategies. Final Report, Research Triangle Institute prepared for Environmental Protection Agency, Research Triangle Park, N.C., EPA Report 450/3-75-036 Task 4.
- Rasmussen, R. A., 1972: What do the hydrocarbons from trees contribute to air pollution? J. Air Poll. Contr. Assoc., 22, 537-543.
- Rasmussen, R. A., et al., 1974: Measurement of light hydrocarbons in the field and studies of transport of oxidant beyond an urban area. Final Report, Contract 68-02-1232, Washington State University, College of Engineering Research Division, Air Pollution Section (in preparation for EPA).
- Rasmussen, R. A., and F. W. Went, 1965: Volatile organic material of plant origins in the atmosphere. Proc. Nat. Acad. Sci., 53, 215.
- Rasmussen, R. A., and E. Robinson, 1975: The role of trace atmospheric constituents in a surface ozone model. Presented at the Annual Meeting, American Meteorological Society, Denver, Colorado.
- Rasmussen, R. A., 1975: Recent field studies as regards the role of NO_x in the oxidant and NO₂ problem. Paper presented at Scientific Seminar on Automotive Pollution, Washington, D.C.
- Rasmussen, R. A., R. B. Chatfield, and M. W. Holden, 1977: Hydrocarbon species in rural Missouri air (unpublished manuscript).
- Reed, R. J., and K. E. German, 1964: A contribution to the problem of stratospheric diffusion by large-scale mixing. Mon. Wea. Rev., 93 (5), 313-321.
- Regener, V. H., and L. Aldaz, 1969: Turbulent transport near the ground as determined from measurements of the ozone flux and the ozone gradient. J. Geophys. Res., 74 (28), 6935-6942.
- Regener, V. H., 1974: Destruction of atmospheric ozone at the ocean surface. Arch. Met. Geoph. Biokl., 23 (ser. A), 131-135.
- Reynolds, S. D., and J. H. Seinfeld, 1975: Interim evaluation of strategies for meeting ambient air quality standards for photochemical oxidant. Env. Sci. and Tech. 9, (5), 435-447.
- Reiter, E. R., and J. D. Mahlman, 1962: Heavy radioactive fallout over the southern United States, November 1962. J. Geophys. Res., 70 (18), 4501-4520.

- Reiter, E. R., M. E. Glasser, and J. D. Mahlman, 1969: The role of the tropopause in stratospheric-tropospheric exchange processes. Pure and Appl. Geophys., 12, 183-221.
- Reiter, E. R., 1975: Stratospheric-tropospheric exchange processes. Rev of Geophys. and Space Phys., 13, 459-474.
- Richter, H. G., 1970: Special ozone and oxidant measurements in vicinity of Mount Storm, West Virginia. Research Triangle Institute, prepared for Environmental Protection Agency, Research Triangle Park, N.C.
- Ripperton, L. A., K. Kornreich, and J.J.B. Worth, 1970: Nitrogen dioxide and nitric oxide in non-urban air. J. Air Poll. Contr. Assoc., 24, (9), 589-592.
- Ripperton, L. A., and F. M. Vukovich, 1971: Gas phase destruction of tropospheric ozone. J. Geophys. Res., 76, 7328-7333.
- Ripperton, L. A., H. Jeffries, and J.J.B. Worth, 1971: Natural synthesis of ozone in the troposphere. Env. Sci. and Tech. 5, 246-248.
- Ripperton, L. A., H. E. Jeffries, and O. White, 1972: Formation of aerosols by reaction of ozone with selected hydrocarbons. Adv. in Chem., 113, 219-231.
- Ripperton, L. A., J.J.B. Worth, C. E. Becker, and D. R. Johnston, 1974: High ozone concentrations in non-urban atmospheres. Presented at 167th ACS Meeting, Los Angeles, California.
- Ripperton, L. A., C. E. Decker, W. C. Eaton, and J. E. Sickles, 1974: The origin of non-urban ozone. Presented at 1974 Annual ACS Meeting, Atlantic City, New Jersey.
- Ripperton, L. A., J. B. Tommerdahl, and J.J.B. Worth, 1974: Airborne ozone measurement. Paper 74-42, Annual Meeting, Air Pollution Control Association.
- Robinson, E., and R. C. Robbins, 1970: Gaseous nitrogen compound pollutants from urban and natural sources. J. Air Poll. Contr. Assoc., 20, 303-306.
- Roth, P. M., P.J.W. Roberts, M. K. Lin, S. D. Reynolds, J. H. Seinfeld, 1974: Mathematical modeling of photochemical air pollution-II. A model and inventory of pollutant emissions. Atm. Env., 8, 97.
- Rubino, R. A., L. Bruckman, and J. Magyar, 1976: Ozone transport. Air Poll. Contr. Assoc., 26, 972-975.
- Schuck, E. A., N. J. Pitts, Jr., and J.K.S. Wan, 1966: Relationships between certain meteorological factors and photochemical smog. Int. J. Air Wat. Poll., 10, 689-711.

- Schuck, E. L., A. P. Altshuller, D. S. Barth, and G. B. Morgan, 1970: Relationship of hydrocarbons to oxidants in ambient atmospheres. J. Air Poll. Contr. Assoc., 20, (5), 297-302.
- Shlanta, A., and C. D. Moore, 1972: Ozone and point discharge measurements under thunder clouds. J. Geophys. Res., 77, 4500-4510.
- Spicer, Chester W., 1976: Ozone and hydrocarbon measurements by Batelle. Proceedings of the Northeast Oxidant Transport Symposium held at Research Triangle Park, North Carolina on January 20-21.
- Stasiuk, N. W., and P. E. Coffey, 1974: Rural and urban ozone relationship in New York State. J. Air Poll. Contr. Assoc., 24, (6), 564-568.
- Staley, D. O., 1960: Evaluation of potential-vorticity changes near the tropopause and the related vertical motions, vertical advection of vorticity, and transfer of radioactive debris from stratosphere to troposphere, J. Meteor., 17, 591-620.
- Staley, D. O., 1962: On the mechanism of mass and radioactivity transport from stratosphere to troposphere. J. Atmos. Sci., 19, 450-467.
- Stephens, E. R., 1969: Chemistry of Atmospheric Oxidants. J. Air. Poll. Contr. Assoc., 19, 181-185.
- Stephens, N. T., and R. O. McCaldin, 1971: Attenuation of power station plumes as determined by instrumented aircraft. Env. Sci. and Tech., 5, 617-621.
- Stephens, E. R., 1975: Chemistry and Meteorology in an Air Pollution Episode. J. Air Poll. Contr. Assoc., 25, (5), 521-524.
- Stickse, P. R., 1976: Occurrence and movement of tropospheric ozone maxima. Proc. Ozone/Oxidant Interactions with the Total Environment Speciality Conference, APCA Southwest Section March, pp. 252-267.
- Stinson, J. R., D. L. Blumenthal, D. S. Gemmill, G. S. Jackson, 1972: Ventilation in the vicinity of Valdez Bay, Alaska. MRI Final Report, FR-1028 to Alyeska Pipeline Service Company, Houston, Texas.
- Stinson, J. R., and J. P. LeBeau, 1972: Hydrocarbon and Ozone Measurements at Valdez, Alaska, between 27 October and 4 November 1972. MRI Special Report R-1058, Alyeska Pipeline Service Company, Houston, Texas.
- Svensson, B. H., and R. Soderlind, eds., 1975: Nitrogen, phosphorus and sulphur - global cycles. Ecological Bulletins/NFR 22, 1-192.
- Tiao, G. C., G.E.P. Box, and W. J. Hamming, 1975: Analysis of Los Angeles photochemical smog data: a statistical overview. J. Air Poll. Contr. Assoc., 25, 260-268.

- Thompson, C. Ray, et al., 1976: Effect of photochemical air pollution on two varieties of alfalfa. Env. Sci. and Tech., 10, 1257-1241.
- Vukovich, F. M., 1973: Some observations of ozone concentrations at night in the North Carolina piedmont boundary layer. J. Geophys. Res., 78, 4458-4462.
- Walker, H. M., 1976: Considerations regarding rural ozone. Proceedings Ozone/Oxidants Interactions with the Total Environment Specialty Conference, APCA Southwest Section March, pp. 268-281.
- Wanta, R. C., W. B. Moreland, and H. E. Heggstad, 1961: Tropospheric ozone: an air pollution problem arising in the Washington, D.C. metropolitan area. Mon. Wea. Rev., 89, 289-296.
- Wayne, L. G., 1961: The Chemistry of Urban Atmospheres, Vol. 3, Los Angeles Control District Technical Program Report, Los Angeles.
- Weinstock, B., and T. Y. Chang, 1976: Methane and nonurban ozone. Presented at the APCA Meeting in Portland, Oregon, June 29.
- Weisman, B., D. H. Matheson, and M. Hirt, 1969: Air pollution survey for Hamilton, Ontario. Atm. Env., 3, 11-23.
- Went, F. W., 1960: Organic matter in the atmosphere and its possible relation to petroleum formations. Proc. N.A.S., Vol. 46, 212.
- Westberg, H., and R. Rasmussen, 1975: Measurement of light hydrocarbons in the field and studies of transport of oxidant beyond an urban area. Progress Report, EPA Contract No. 68-02-1232.
- Westberg, H., K. J. Allwine, and D. Elias, 1976: Vertical Ozone Distribution Above Several Urban and Adjacent Rural Areas Across the United States. Proc. Ozone/Oxidant Interactions with the Total Environment Speciality Conference, APCA Southwest Section March.
- Westberg, H., 1976: Ozone and hydrocarbon measurements by W.S.U. Proceedings of the Northeast Oxidant Transport Symposium held at Research Triangle Park, North Carolina on January 20-21.
- White, W. H., et al., 1976: Formation and transport of secondary air pollutants: ozone and aerosols in the St. Louis urban plume. Science, 194, 187-189.
- Williams, J. D., J. R. Farmer, R. B. Stephenson, G. G. Evans, and R. B. Dalton, 1968: Air pollutant emissions related to land area--a basis for a preventive air pollution control program. NAPCA Publication APTD-68-11.
- Wolff, G. T., 1974: Implications of photochemical oxidants in the New Jersey-New York-Connecticut AQCR. APCA Paper 74-35.3, Air Pollution Control Association Annual Meeting, Denver, Colorado.

Wolff, G. T., et al., 1976: Aerial investigation of the ozone plume phenomenon, J. of Air Poll. Control Assoc. (in press).

Worth, J.J.B., L. A. Ripperton, and C. R. Barry, 1967: Ozone variability in mountain terrain. J. Geophys. Res., 72, 2063-2068.